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copper oxide was very dark brown, not black. Tests performed on the oxide showed it to be free from impurity.

A saturated solution of purified copper sulphate ( $14.5^{\circ}$ ) was diluted with an equal volume of distilled water, and to the cold solution was added a cold ( $14.5^{\circ}$ ) solution of pure sodium carbonate (10 per cent.). The precipitate was allowed to remain for twenty-four hours, and then washed on a Büchner funnel with distilled water until free from sulphate. The precipitate, on solution, contained no sulphate. It was dried in a steam-oven at  $96^{\circ}$  until its weight was constant.

TABLE III.

	CuO per cent.	CO <sub>2</sub> per cent.	H <sub>2</sub> O per cent.	Total per cent.
The average composition of the precipitate was	72.98	15.46	11.89	100.33
13CuO, 5CO <sub>2</sub> , 9H <sub>2</sub> O requires	73.02	15.54	11.44	100.00
Pickering's compound 8CuO, 3CO <sub>2</sub> , 6H <sub>2</sub> O requires	72.62	15.06	12.32	100.00

The above percentages give the formula:  $13.07\text{CuO}, 5\text{CO}_2, 9.40\text{H}_2\text{O}$ .

*The Basic Carbonate*,  $2\text{CuCO}_3, 5\text{Cu}(\text{OH})_2$  or  $7\text{CuO}, 2\text{CO}_2, 5\text{H}_2\text{O}$ .

A solution of pure copper sulphate, saturated at  $14.5^{\circ}$ , was diluted with an equal quantity of distilled water, and to this solution was added a solution containing 5 per cent. of sodium carbonate and 5 per cent. of sodium hydrogen carbonate. The carbonate solution was added with stirring until, on filtering a small portion, the filtrate gave no precipitate with it. The mixture was allowed to remain until next day, and was then filtered on a Büchner funnel and washed free from sulphate. This required

TABLE IV.

	CuO per cent.	CO <sub>2</sub> per cent.	H <sub>2</sub> O per cent.	Total per cent.
a. Mean of three analyses	75.90	11.25	12.78	99.93
b) Mean of four analyses	75.48	11.55	13.18	100.21
c) Mean of three analyses	75.39	12.04	12.88	100.31
Mean	75.59	11.61	12.95	100.15
CuCO <sub>3</sub> , 5Cu(OH) <sub>2</sub> requires	75.77	11.98	12.25	100.00

Stated as formulæ the above results become:—

- (a)  $7\text{CuO}, 1.89\text{CO}_2, 5.20\text{H}_2\text{O}$ .
- (b)  $7\text{CuO}, 1.93\text{CO}_2, 5.39\text{H}_2\text{O}$ .
- (c)  $7\text{CuO}, 2.01\text{CO}_2, 5.28\text{H}_2\text{O}$ .
- Mean:  $7\text{CuO}, 1.94\text{CO}_2, 5.29\text{H}_2\text{O}$ .
- Theory:  $7\text{CuO}, 2.00\text{CO}_2, 5.00\text{H}_2\text{O}$ .



many hours, and usually extended until the next morning. The wet precipitate was then allowed to remain until the third day and dried in a steam-oven. The drying process never lasted less than six hours.

Three separate preparations, (a), (b), and (c), were made. The analyses of these preparations are shown in table IV (p. 721).

#### Summary.

Examination of a number of samples of commercial copper carbonate gave evidence to show that the statement that it has the same composition as malachite is erroneous.

An attempt has been made to prepare a basic copper carbonate of approximately constant composition from pure materials.

A new basic copper carbonate,  $2\text{CuCO}_3 \cdot 5\text{Cu}(\text{OH})_2$  or  $7\text{CuO} \cdot 2\text{CO}_2 \cdot 5\text{H}_2\text{O}$ ,

is described.

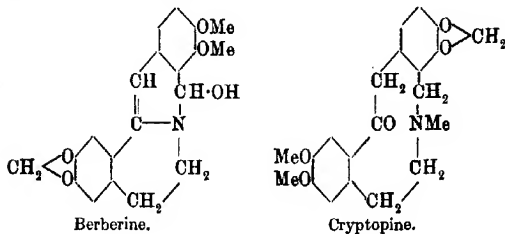
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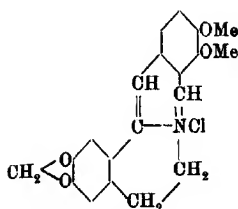
[Received, April 25th, 1918.]

### LXV.—A Study of some Derivatives of Berberine Closely Allied to Derivatives of Cryptopine.

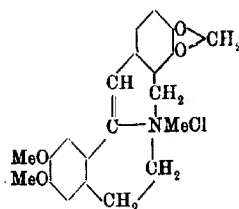
By WILLIAM HENRY PERKIN, jun.

THE close relationship which exists between berberine and cryptopine has been discussed on more than one occasion (compare T., 1916, 109, 833, 841; this vol., p. 493), and it has been pointed out that, if the formulæ of the alkaloids, or better still of their quaternary salts, are written side by side, it is readily seen that the difference between the two is, in the main, the presence of the *N*-methyl group in cryptopine and its absence in the berberine



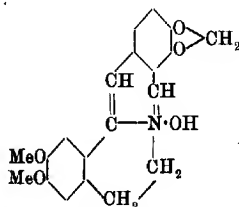


Berberinium chloride.

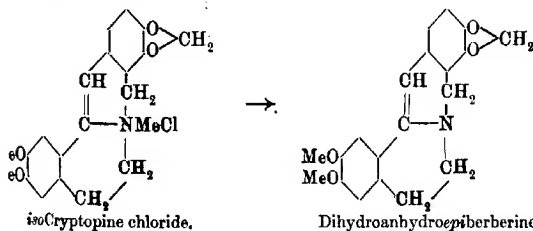


isocryptopine chloride.

molecule, and the fact that the positions of the two methoxy-groups and the methylenedioxy-group are reversed in the two formulæ. It was further pointed out that the alkaloid of the berberine type which actually corresponds with cryptopine is *epiberberinium* hydroxide,

*epi*Berberinium hydroxide.

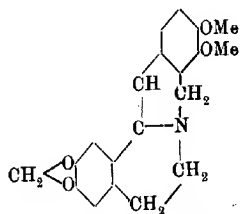
and the conversion of cryptopine into this interesting alkaloid has recently been described (this vol., p. 493). The problem which had to be solved in attempting the preparation of *epiberberine* from cryptopine was essentially the discovery of some method which would render possible the removal of the *N*-methyl group from the latter alkaloid, and this difficult step was ultimately accomplished by heating *isocryptopine* chloride at 280°, when methyl chloride was eliminated according to the scheme:

*isocryptopine* chloride.Dihydroanhydro*epiberberine*.

*epi*dihydroanhydro*epiberberine* obtained in this way served as principal source from which a considerable number of derivatives of *epiberberine* were subsequently obtained and examined.

The object of the present investigation was to accomplish the reverse change, namely, to introduce an *N*-methyl group into the berberine molecule in order to study derivatives of berberine which were similarly constituted to corresponding derivatives of cryptopine, and only differed from these in containing the two methoxy-groups and the methylenedioxy-group in the reversed positions. It was hoped that results might be obtained in this way that would confirm and amplify certain curious observations made during the study of the derivatives of cryptopine, and this has proved to be the case.

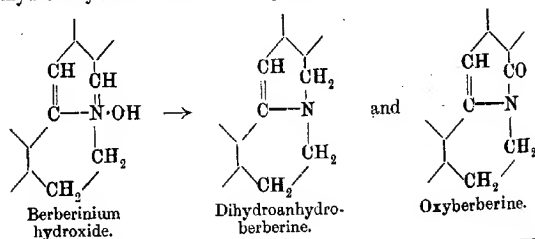
The substance most largely employed for the purposes of this investigation has been dihydroanhydroberberine,\*



Dihydroanhydroberberine.

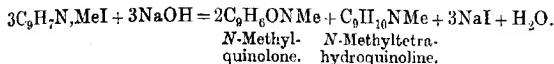
and the opportunity was taken to bring forward additional evidence in support of the identity and constitution of this important substance.

Dihydroanhydroberberine was first obtained by Gadamer (*Arch. Pharm.*, 1905, **243**, 35) during the course of a valuable investigation into the action of alkalis on berberinium hydroxide. Gadamer showed that berberinium sulphate or hydroxide, when heated on the steam-bath with concentrated sodium hydroxide solution, undergoes simultaneous reduction and oxidation with the formation of dihydroanhydroberberine and oxyberberine:



\* With regard to the nomenclature employed in this communication for berberine and its derivatives, compare this vol., p. 503.

According to Gadamer, dihydroanhydroberberine melts at 165—167°, crystallises in deep yellowish-brown tablets, yields a hydrochloride,  $C_{20}H_{19}O_4N.HCl.3H_2O$ , and is readily oxidised on exposure to the air to berberine. At a later date (*Monatsh.*, 1910, **31**, 557), Faltis expressed the opinion that the reaction between berberinium hydroxide and sodium hydroxide was not analogous to the Cannizzaro reaction between aromatic aldehydes and alkali, but was similar to the change which Decker (*Ber.*, 1903, **36**, 2568) has observed to take place when quinoline methiodide is treated with an alkali:



In other words, Faltis was of opinion that the substance which Gadamer had described as dihydro(anhydro)berberine was in reality tetrahydro(anhydro)berberine. That such a suggestion could have been made is remarkable, for, with the exception of almost identical melting points (168—170°), there are scarcely any points of resemblance between dihydroanhydroberberine and tetrahydroanhydroberberine. Tetrahydroanhydroberberine is colourless and gives colourless salts, of which the hydrochloride has the composition  $C_{20}H_{21}O_4N.HCl$ ; dihydroanhydroberberine has a striking, yellowish-brown colour and yields a deep yellow hydrochloride,  $C_{20}H_{19}O_4N.HCl.3H_2O$ . The mistaken view which Faltis advanced is doubtless partly due to the fact that he used impure dihydroanhydroberberine for his experiments, for he states (*loc. cit.*, p. 567) that the material that he employed melted at 135—155°, whereas pure dihydroanhydroberberine melts at 166—168°.

Faltis further makes the erroneous statement that there is no depression in melting point when equal quantities of dihydroanhydroberberine and tetrahydroanhydroberberine are mixed, whereas the present author finds that such a mixture of the pure substances softens at 140—145°, and is completely melted at 152°. Faltis did not make any comparative analyses of dihydroanhydroberberine and tetrahydroanhydroberberine, or he would have suspected that these substances could not be identical, since the former,  $C_{20}H_{19}O_4N$ , contains  $C=71.2$ ,  $H=5.6$ , whereas the latter,  $C_{20}H_{21}O_4N$ , contains  $C=70.8$ ,  $H=6.2$ , a difference quite easily detected by accurate analysis (compare p. 739). The only positive evidence which Faltis brings forward in support of his view that these bases are identical is that they require approximately equal amounts of iodine to oxidise them to berberine. A method of this kind carried out under the conditions observed by Faltis would be

open to grave suspicion in any case, and is obviously quite valueless when impure material is employed in the determinations.

The contention that dihydroanhydroberberine and tetrahydroanhydroberberine are identical was subsequently dealt with by Gadamer (*Arch. Pharm.*, 1910, **248**, 670), who not only discussed in detail the points raised by Faltis and showed that they are groundless, but also brought forward further and convincing evidence that the substance described by him as dihydro(anhydro)berberine is in fact that substance.

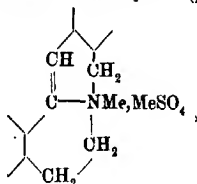
The results of the present investigation indirectly confirm the identity of dihydroanhydroberberine, and additional positive evidence has arisen from the observation that it is possible to grow crystals of this substance and also of tetrahydroanhydroberberine from acetone which are suitable for crystallographical examination. The measurement of these crystals, which was kindly undertaken by Miss M. W. Porter (p. 741), clearly proves that these substances cannot possibly be identical.

In only one point does the experience of the author in connexion with dihydroanhydroberberine differ from the accurate statements of Gadamer. Gadamer frequently mentions that this base and its salts are easily oxidised by exposure to air and converted into berberine and its salts. The present author, on the other hand, cannot confirm this ready oxidisability. A specimen of the pure hydrochloride which had remained on porous porcelain in a drawer exposed to air for more than six months yielded the same analytical results as before exposure, and the solution of a weighed quantity in water gave, on the addition of ammonia, a precipitate of dihydroanhydroberberine which was nearly the amount which should have been obtained from the pure hydrochloride (p. 740). If conversion of the hydrochloride into berberinium chloride had taken place during exposure, there would either have been no precipitate on the addition of ammonia or, in the event of partial change, a diminished yield. Again, a specimen of pure dihydroanhydroberberine which had been several times recrystallised from acetone and melted at 167–168° was left on a watch-glass exposed to the air for six months without apparent change. At the end of this time, the specimen melted at the same temperature as before exposure and yielded the same analytical results, an experience which is in accord with the statement of Gadamer that a specimen of dihydroanhydroberberine, crystallised from ether, which he had prepared in 1902, still showed the same melting point in 1910 as when first prepared. It seems therefore clear that dihydroanhydroberberine is not readily oxidised by contact with air, and this is in harmony with the behaviour observed in the analogous case of

dihydroanhydroepiberberine (this vol., p. 507), which also may be exposed to the air for a long time without apparent change.

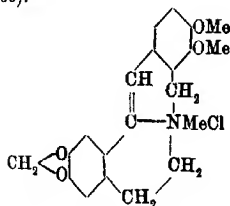
*Dihydroanhydroberberine Methosulphate and its Conversion into Anhydromethylberberine.*

The basis of the experiments chronicled in the following pages is *dihydroanhydroberberine methosulphate* (p. 743),

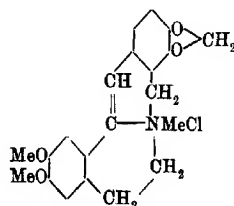


which is readily prepared by the direct combination of dihydroanhydroberberine with methyl sulphate, and separates from methyl alcohol in brilliant yellow, orthorhombic prisms melting at 205°.

The corresponding *methiodide*,  $C_{20}H_{19}O_4N, MeI$  (m. p. 215–220°), which is obtained from the methosulphate by precipitation with potassium iodide, had already been described by Freund and Fleischer (*Annalen*, 1915, **409**, 231), who prepared it by the direct addition of methyl iodide to dihydroanhydroberberine. *Dihydroanhydroberberine methochloride*,  $C_{20}H_{19}O_4N, MeCl$  (m. p. 223°), obtained by digesting the iodide with water and silver chloride, separates from water, apparently with 5H<sub>2</sub>O, in pale yellow prisms. This methochloride has been made the subject of special inquiry on account of its close relationship to *isocryptopine chloride* (833).\*



Dihydroanhydroberberine methochloride.



*iso*Cryptopine chloride.

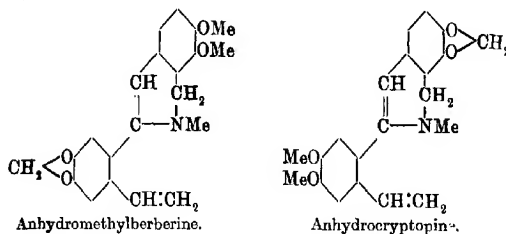
These so closely allied quaternary chlorides exhibit, as was to be expected, great similarity in their properties and reactions. They

\* The numbers in brackets—thus (833)—refer to the paper on Cryptopine and Protopine (T., 1916, **109**, 815–1028).

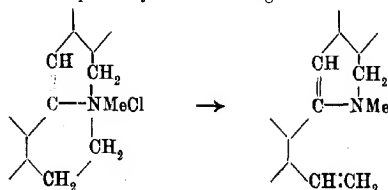
are both characterised by sparing solubility in dilute hydrochloric acid, although dihydroanhydroberberine methochloride is more readily soluble both in water and dilute hydrochloric acid than *isocryptopine* chloride.

Interesting results have been obtained from the study of the reduction of dihydroanhydroberberine methochloride, and these are described on p. 732. The behaviour of *isocryptopine* chloride under the same conditions has also been investigated, and will form the subject of a future communication.

*Anhydromethylberberine*.—This interesting substance corresponds in its method of preparation and in its properties with anhydrocryptopine (850), the relationship between the two substances being at once evident when their formulae are written side by side:



Just as anhydrocryptopine results from the action of methyl-alcoholic potassium hydroxide on *isocryptopine* chloride, so dihydroanhydroberberine methochloride yields anhydromethylberberine when it is decomposed by the same reagent:

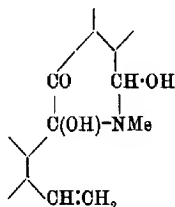


The process actually used in the preparation of most of the anhydromethylberberine required for the present investigation was the direct decomposition of dihydroanhydroberberine methosulphate by boiling with methyl-alcoholic potassium hydroxide (p. 746).

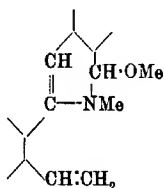
*Anhydromethylberberine*,  $C_{21}H_{21}O_4N$ , melts at  $94-95^\circ$  (anhydrocryptopine at  $110-111^\circ$ ) and separates from methyl alcohol in pale yellow prisms.

Like anhydrocryptopine, it is a rather weak base, since the

acetate, for example, is dissociated by water, but the salts with mineral acids are stable in the presence of excess of acid. It undergoes a curious change when its solution in methyl alcohol is slowly evaporated in contact with air, yielding, besides a large quantity of a brittle resin, a small amount of a crystalline substance,  $C_{21}H_{21}O_7N$  (p. 747), which melts at  $153-155^\circ$ , has no basic properties, and is probably a *trioxyanhydromethylberberine* containing the grouping:

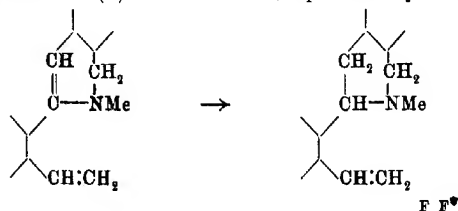


In this respect, anhydromethylberberine appears to behave differently from anhydrocryptopine, since the latter, when boiled with methyl alcohol in contact with air, yields by the addition of methyl alcohol and simultaneous oxidation, large quantities of the two isomeric methoxyanhydrocryptopines (*A*) and (*B*) (856), which contain the grouping:



It is, of course, possible that substances corresponding with the two modifications of methoxyanhydrocryptopine are contained in the resin which is the main product of the action of methyl alcohol and air on anhydromethylberberine, but attempts to isolate such substances in a crystalline condition have been unsuccessful.

*Reduction of Anhydromethylberberine to N-Methylisotetrahydroanhydroberberine (B).—*This reduction, represented by the scheme





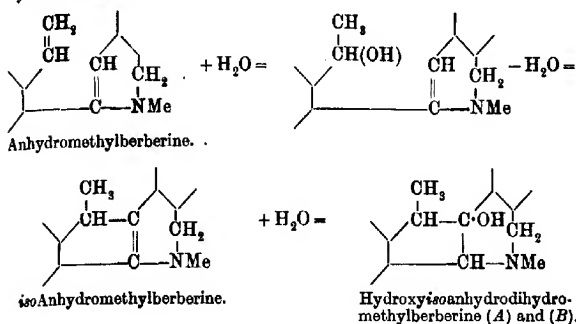
corresponds exactly with the reduction of anhydrocryptopine (989) to anhydrosdihydrocryptopine (*B*). The addition of hydrogen takes place readily when the solution of anhydromethylberberine in dilute sulphuric acid is treated with sodium amalgam (p. 748), and, on adding ammonia, a base separates which melts at 112–113° and is identical with *N*-methylisotetrahydroanhydroberberine (*B*) which Pyman (T., 1913, 103, 827) obtained from tetrahydroanhydroberberine methohydroxide by evaporation under atmospheric pressure. The similarity in constitution and properties between the anhydrosdihydrocryptopines and *N*-methylisotetrahydroanhydroberberines has already been fully discussed (841), and the preparation of dihydroanhydroberberine methochloride and its conversion first into anhydromethylberberine and then into *N*-methylisotetrahydroanhydroberberine now completes the picture.

*The Action of Hydrochloric Acid on Anhydromethylberberine.*

*Formation of the Hydroxyisoanhydrosdihydromethylberberines (A) and (B).*

A highly characteristic property of anhydrocryptopine is the brilliant crimson colour which is produced when this substance is boiled with concentrated hydrochloric acid (865), and the same colour is produced in less degree when anhydromethylberberine is treated in the same manner. In the case of the action of concentrated hydrochloric acid on anhydrocryptopine, it was found possible to isolate two crystalline products, namely, the *epicryptopines* (*A*) and (*B*), but attempts to obtain similar products in crystalline condition from the product of the interaction of anhydromethylberberine and concentrated hydrochloric acid have been unsuccessful. On the other hand, another reaction, highly characteristic of anhydrocryptopine, namely, its behaviour towards dilute hydrochloric acid, is reproduced exactly when anhydromethylberberine is subjected to the action of dilute hydrochloric acid under the same conditions. When anhydrocryptopine is heated with dilute hydrochloric acid (860), it is converted, by the addition of water into the stereoisomeric hydroxyisoanhydrosdihydrocryptopines (*A*) and (*B*), which melt at 227° and 117° respectively, and the probable course of the reaction and constitution of these substances has already been fully discussed (862). Anhydromethylberberine is very readily acted on by hot dilute hydrochloric acid (p. 752), and yields, as the result of the addition of water, two isomeric hydroxyisoanhydrosdihydromethylberberines, (*A*) and (*B*), which melt respectively at 210–212° and 168–170°. Since these

substances behave in all their properties exactly like the hydroxy-*isoanhydro*dihydrocryptopines, there can be little doubt that they also are stereoisomeric, and that their formation may be expressed by the scheme:



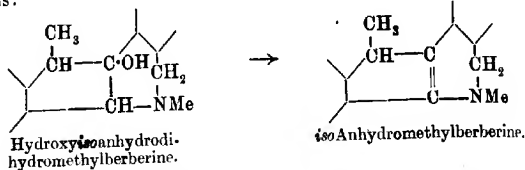
The hydroxy*isoanhydro*dihydromethylberberines (A) and (B) react very readily with acetyl chloride, and the result of the interaction is the same in either case. The product is a mixture of the hydrochlorides,  $\text{C}_{21}\text{H}_{22}\text{O}_5\text{NAc.HCl}$ , of two *acetoxyisoanhydro*dihydromethylberberines, one of which is more readily soluble than the other. The more sparingly soluble hydrochloride (m. p.  $253^\circ$ ) yields, on decomposition with ammonia, the acetyl derivative,  $\text{C}_{21}\text{H}_{22}\text{O}_5\text{NAc}$ , which melts at  $165\text{--}167^\circ$ , together with some hydroxy*isoanhydro*dihydromethylberberine (A) produced by hydrolysis. It would therefore appear that the substance melting at  $165\text{--}167^\circ$  is *acetoxyisoanhydrodihydromethylberberine* (A).

The more readily soluble hydrochloride gives, with ammonia, an acetyl base,  $\text{C}_{21}\text{H}_{22}\text{O}_5\text{NAc}$ , which melts at  $213\text{--}215^\circ$ , and is presumably *acetoxyisoanhydrodihydromethylberberine* (B). It is, however, difficult to be certain as to the identity of these acetyl derivatives, since, on boiling with dilute hydrochloric acid, both yield a mixture of the two hydroxy*isoanhydro*dihydromethylberberines (A) and (B).

#### *isoAnhydromethylberberine.*

In connexion with the investigation of the hydroxy*isoanhydro*dihydrocryptopines (A) and (B) (861), it was pointed out that one of the most characteristic properties of these stereoisomerides is the conversion into *isoanhydro*cryptopine (m. p.  $158\text{--}160^\circ$ ), a change which both undergo when they are boiled with concentrated

hydrochloric acid or digested with phosphoryl chloride. The (A) and (B) modifications of hydroxyisoanhydromethylberberine behave in an exactly similar manner (p. 756) and yield isoanhydromethylberberine,  $C_{21}H_{21}O_4N$ , which, like the corresponding cryptopine derivative, crystallises beautifully in glistening prisms and melts at 123–124°. The formation of this substance from the hydroxyisoanhydromethylberberines is due to dehydration, and the change is probably correctly represented thus:



iso. 1*Anthromethylberberine* yields well-defined, sparingly soluble salts, of which the hydrochloride,  $C_{21}H_{21}O_4N \cdot HCl$  (m. p. 205–210°), and the hydriodide,  $C_{21}H_{21}O_4N \cdot HI$  (m. p. 247°), were prepared and analysed.

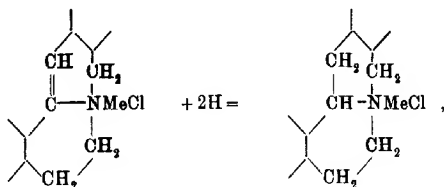
When the sulphate is boiled with excess of dilute sulphuric acid, hydration occurs, and two substances,  $C_{21}H_{23}O_5N$ , are produced which melt at  $215^\circ$  and  $165-167^\circ$  respectively.

These consist of the (A) and (B) modifications of hydroxyisoanhydrodihydromethylberberine, and the production of these modifications, in this manner, is strong evidence that the view of their formation from anhydromethylberberine advanced on p. 731 is correct.

*Reduction of Dihydroanhydroberberine Methochloride.*

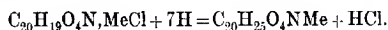
The interesting behaviour of dihydroanhydroberberine methochloride on reduction in boiling dilute hydrochloric acid solution with sodium amalgam has been made the subject of an extended investigation (p. 758), partly with the view of comparing the results with those obtained from the study of the reduction of isocryptopine chloride under the same conditions, an investigation which it is hoped will form the subject of a future communication. Under the conditions mentioned, dihydroanhydroberberine methochloride yields a quaternary chloride (a) and the hydrochloride (b) of a new base. The quaternary chloride (a), produced by the addition of two atoms of hydrogen to the double linking, can be separated by fractional crystallisation into two substances melting at 245–250° and 280–285° respectively, and these are identical with

the ( $\alpha$ -) and ( $\beta$ -) modifications of the methochloride of tetrahydroanhydroberberine first prepared by Pyman (T., 1913, 103, 825, 826) by the addition of methyl iodide to tetrahydroanhydroberberine and subsequent treatment with silver chloride. The reduction of dihydroanhydroberberine methochloride in this case has therefore proceeded in a simple manner according to the scheme:

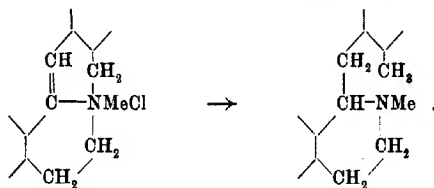


a process which creates an asymmetric carbon atom, and thus allows of the formation of stereoisomeric methochlorides, because the molecule already contains an asymmetric centre, namely, the nitrogen atom attached to five different groups.

The base from the hydrochloride (*b*) is a syrup, has the composition  $\text{C}_{27}\text{H}_{25}\text{O}_4\text{N}$ , and has therefore been produced from dihydroanhydroberberine methochloride according to the equation

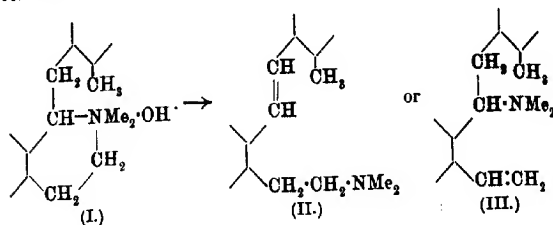


The comparison of the properties of this base with those of a similar but better characterised base, which has been obtained by the reduction of *isocryptopine* chloride, leaves little doubt that its formation is correctly expressed in the following manner:



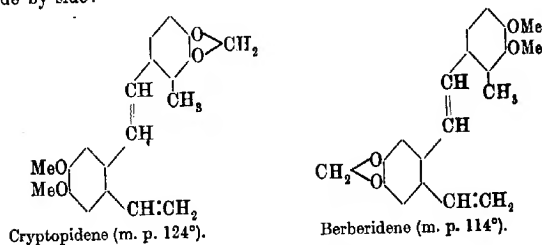
This base is therefore *dihydromethylisotetrahydroanhydroberberine* (compare Pyman, T., 1913, 103, 828). It combines readily with methyl sulphate, and the resulting methosulphate is decomposed by boiling with methyl-alcoholic potassium hydroxide (p. 760), with the formation of *dihydrodimethylisotetrahydroanhydroberberine*,  $\text{C}_{29}\text{H}_{27}\text{O}_4\text{N}$  (950). There are two directions in which the elimination of water from the methohydroxide (I) may

take place, leading to the formation of substances represented by formulæ II or III:



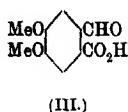
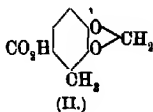
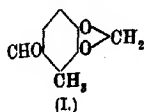
The mechanism of the change is, in both cases, so similar that there seems no reason why the process should take one direction rather than the other. Arguing, however, again from the analogous behaviour of *isocryptopine* chloride in the same circumstances—in which case it has been clearly demonstrated that the substance produced by the elimination of water from the methohydroxide corresponding with I has formula II, and not III—there is every reason to suppose that the formula of dihydrodimethylisotetrahydroanhydroberberine is that represented by II. This syrupy base yields a crystalline methosulphate,  $\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4$ , which, on boiling with methyl-alcoholic potassium hydroxide, readily loses trimethylamine and water and yields a beautifully crystalline substance,  $\text{C}_{20}\text{H}_{20}\text{O}_4$ , which melts at  $113\text{--}114^\circ$ .

Careful investigation of this substance has shown that it is completely analogous to cryptopidene (827), and it has therefore been named '*berberidene*.' The intimate relationship between these two substances is well brought out when their formulæ are written side by side:

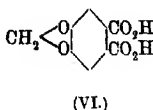
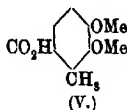
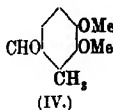


The main evidence in support of the formula assigned to cryptopidene was derived from the study of its behaviour on oxidation, when it yielded 5:6-methylenedioxy-*o*-tolualdehyde (I) and 5:6-methylenedioxy-*o*-toluic acid (II) from the upper part of the mole-

cule and 4:5-dimethoxy-2-aldehydobenzoic acid (*m*-opianic acid, III) from the lower section:



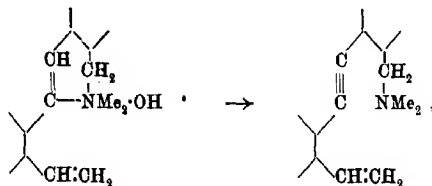
When berberidene was subjected to oxidation, in acetone solution with permanganate (p. 762) in exactly similar circumstances, it yielded 5:6-dimethoxy-*o*-tolualdehyde (IV), 5:6-dimethoxy-*o*-toluic acid (V), from the upper, and an acid melting at 174–176°, which was doubtless hydrastic acid (VI), from the lower part of the molecule:



The formation of these substances is obviously in complete harmony with the constitution assigned above to berberidene.

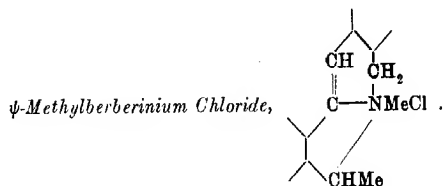
*Anhydromethylberberine Methosulphate and ψ-Methylberberinium Chloride.*

Anhydrocryptopine combines readily with methyl sulphate, yielding a colourless, crystalline methosulphate (978) which resembles other methosulphates in many of its reactions, but is characterised by the remarkable fact that it is decomposed by alkalis with regeneration of anhydrocryptopine, whereas normally the methyl derivative should have resulted. Attempts to explain the unusual course of this decomposition were made at the time (854), but it was not then pointed out that if the reaction had proceeded normally it would have led to the formation of a substance containing a triple bond, and it is possible that the disinclination to

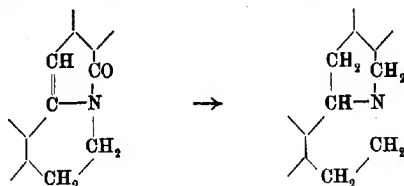


form such a substance may be very great and is perhaps a factor in bringing about the abnormal decomposition of the methosulphate.

In view of the unusual properties exhibited by anhydrocryptopine methosulphate, it was clearly of interest to ascertain whether anhydromethylberberine would yield a methosulphate which would behave in a similar manner. This has been found to be the case. Anhydromethylberberine,  $C_{21}H_{21}O_4N$ , combines readily with methyl sulphate, and the resulting methosulphate,  $C_{21}H_{21}O_4N, Me_2SO_4, H_2O$ , crystallises from water in colourless needles melting at  $150-152^\circ$ . The *methiodide*,  $C_{21}H_{21}O_4N, MeI$ , obtained from the methosulphate by precipitation with potassium iodide, closely resembles anhydrocryptopine methiodide in appearance and general properties, and it is curious that both melt at the same temperature ( $188-190^\circ$ ). When anhydromethylberberine methosulphate is digested with methyl-alcoholic potassium hydroxide, decomposition occurs readily and a substance separates which, after crystallisation from methyl alcohol, melts at  $92-94^\circ$  and consists of anhydromethylberberine, the yield being almost quantitative. In this decomposition, anhydromethylberberine methosulphate behaves in precisely the same unusual way as anhydrocryptopine methosulphate.



Just as  $\psi$ -cryptopine chloride (m. p.  $110^\circ$ ) results from the action of boiling concentrated hydrochloric acid on anhydrocryptopine methosulphate (984), so the same process applied to anhydromethylberberine methosulphate leads to the formation of  $\psi$ -methylberberinium chloride,  $C_{21}H_{22}O_4NCl, H_2O$ . This interesting quaternary chloride closely resembles  $\psi$ -cryptopine chloride in its curious colour reactions and other properties (p. 751). It crystallises well from dilute hydrochloric acid, melts at about  $95-100^\circ$ , and yields, when its aqueous solution is mixed with potassium iodide,  $\psi$ -methylberberinium iodide,  $C_{21}H_{22}O_4NI$ , which melts at  $175-180^\circ$ .

*Reduction of Oxyberberine to Tetrahydroanhydroberberine,*

The synthesis of oxyberberine was accomplished by Pictet and Gams in 1911 (*Compt. rend.*, **152**, 1102), but as these investigators were unable to reduce oxyberberine to tetrahydroanhydroberberine, which, on oxidation in acid solution, would in turn yield salts of berberine, they were obliged to devise another method in order to complete the synthesis of the salts of berberine (*Compt. rend.*, 1911, **153**, 386; *Ber.*, 1911, **44**, 2480). The present author finds, however, that oxyberberine may be readily reduced electrolytically to tetrahydroanhydroberberine under the conditions given on p. 764. It follows, therefore, that the synthesis of oxyberberine by Pictet and Gams is now also a synthesis of berberine

## EXPERIMENTAL.

*The Action of Sodium Hydroxide on Berberinium Chloride.**Preparation of Oxyberberine and Dihydroanhydroberberine.*

The conversion of berberinium sulphate into oxyberberine and dihydroanhydroberberine by heating with sodium hydroxide was first observed by Gadamer (*Arch. Pharm.*, 1905, **243**, 35), and at a later date (*ibid.*, 1910, **248**, 676) more complete details of the process and of the isolation of the products were given by the same investigator. The method recommended is, however, a tedious one and has the disadvantage that the isolation of the products not only entails a large number of operations, but necessitates the use of large volumes of ether.

Since considerable quantities of dihydroanhydroberberine were required for the present research, the author has carried out a series of comparative experiments on the action of sodium hydroxide on berberinium chloride (which is more accessible than the sulphate), and, as the result, the following procedure has been adopted for the preparation of dihydroanhydroberberine and oxyberberine. Commercial berberine hydrochloride (berberinium



chloride, 500 grams) is thoroughly mixed with aqueous sodium hydroxide (700 c.c. of 30 per cent.) in a stout, round-bottomed flask and left for half an hour. The flask is then suspended in a large enamelled basin full of cold water, and the basin slowly heated over a ring burner in such a manner that the water comes to the boil in about half an hour, and it is better not to stir at this stage. The heating is continued for an hour, during which the viscid, dark brown mass may be shaken round repeatedly so as to bring it into better contact with the alkali. On keeping overnight, the black, syrupy layer will have solidified; the aqueous alkali is then run off, the mass washed in the flask with water by decantation, and mixed with dilute hydrochloric acid until the whole is strongly acid. After heating on the steam-bath and filtering by the aid of the pump, the residue is ground up and the treatment with hot dilute hydrochloric acid repeated until all the basic substance has been extracted and a nearly colourless mass of oxyberberine remains.

The different extracts are mixed, while still hot, with concentrated hydrochloric acid, when, on keeping, a large crop of crystals separates which consists of the hydrochloride of dihydroanhydroberberine mixed with varying quantities of unchanged berberinium chloride.

The crops of crystals from the hydrochloric acid extracts, obtained as described above, are collected, washed with dilute hydrochloric acid to remove the dark greenish-brown solution, and recrystallised by dissolving in the least quantity of boiling water and adding concentrated hydrochloric acid. After being collected, the crystals are dissolved in hot water and mixed with excess of ammonia, when a dark brown, semi-solid mass separates which soon hardens. This is ground up and washed by the aid of the pump with hot water until the filtrate is no longer dark purplish-brown;\* the residue is then left on porous porcelain until dry. In order to

\* The intensely coloured filtrate deposits, on keeping, a splendid chocolate coloured salt which crystallises from hot water in brilliant chocolate coloured needles and was at first thought to be a new substance. In this condition the salt had the remarkable property of dissolving in boiling dilute hydrochloric acid to an orange solution and separating in deep orange needles. Even after repeated recrystallisation from dilute hydrochloric acid, the salt retained the peculiarity of dissolving in boiling dilute ammonia to an intense purple solution from which chocolate coloured needles separated on cooling. However, after repeated crystallisation from methyl alcohol, the salt lost this property and was found to consist of berberinium chloride, since it yielded oxyberberine and dihydroanhydroberberine with sodium hydroxide. The methyl-alcoholic mother liquors contain the highly coloured substance and, when the solution is concentrated, this separates, mixed with berberinium chloride, in almost black needles, the nature of which has not been determined.

purify this crude dihydroanhydroberberine, the best plan is to triturate it with methyl alcohol, in which it is sparingly soluble, then to transfer to the filter and wash with methyl alcohol until the intensely red impurity has been removed, and finally to repeat the same process with acetone. The residue melts at 163–166° and is dihydroanhydroberberine of good quality; after two crystallisations from acetone the substance is quite pure (m. p. 168–170°). The acetone liquors from the washing and crystallisations of the crude dihydroanhydroberberine yield, on concentration, a further crop, which is, however, very dark coloured, and the better plan is to distil off the acetone and dissolve the dark syrup in boiling dilute hydrochloric acid. The solution is mixed with concentrated hydrochloric acid, the hydrochloride which separates on keeping is recrystallised and worked up for dihydroanhydroberberine exactly as already described. Since Faltis (*Monatsh.*, 1910, **31**, 565) has stated that the substance obtained in the decomposition of a berberinium salt with sodium hydroxide is not dihydroanhydroberberine,  $C_{20}H_{19}O_4N$ , but tetrahydroanhydroberberine,  $C_{20}H_{21}O_4N$ , three different preparations were analysed:

0.1142 gave 0.2970  $CO_2$  and 0.0581  $H_2O$ .  $C=70.9$ ;  $H=5.6$ .

0.1075 „ 0.2805  $CO_2$  „ 0.0550  $H_2O$ .  $C=71.2$ ;  $H=5.7$ .

0.1161 „ 0.3032  $CO_2$  „ 0.0591  $H_2O$ .  $C=71.3$ ;  $H=5.7$ .

$C_{20}H_{19}O_4N$  requires  $C=71.2$ ;  $H=5.6$ .

$C_{20}H_{21}O_4N$  requires  $C=70.8$ ;  $H=6.2$  per cent.

*Dihydroanhydroberberine* melts, according to Gadamer, at 169–170°, and the specimens used in the above analyses all melted when moderately rapidly heated at 168–170°. An intimate mixture of approximately equal amounts of dihydroanhydroberberine and tetrahydroanhydroberberine (m. p. 170°) softened at 140–145° and was completely melted at 152°, so that there can be no question of their identity.

Dihydroanhydroberberine is sparingly soluble in methyl alcohol or acetone, even on boiling, but dissolves more readily in boiling ethyl alcohol. It is rather readily soluble in boiling benzene, from which it crystallises well in yellow prisms. The solution in acetic acid does not give a characteristic coloration on the addition of sulphuric acid, but the addition of a trace of dilute nitric acid causes a deep brown to develop.

In view of the fact that anhydromethylberberine (p. 730) is so readily changed by boiling with hydrochloric acid, and this substance and dihydroanhydroberberine are so similarly constituted it seemed desirable that the behaviour of dihydroanhydroberberine towards hydrochloric acid should also be investi-

gated. The powdered base dissolves readily when mixed with concentrated hydrochloric acid and heated to boiling by means of a sulphuric-acid bath, and the deep yellow solution becomes paler as the boiling continues. After ten minutes, the hydrochloric acid was boiled off, leaving a yellow syrup which, on the addition of water, immediately crystallised in yellow needles, and these consisted of dihydroanhydroberberine hydrochloride. The solution of the salt in warm water gave with ammonia the free base, which, after crystallisation from methyl alcohol, melted at  $168^{\circ}$  and consisted of dihydroanhydroberberine.

*The Stability of Dihydroanhydroberberine and its Salts when exposed to Air.*—It is pointed out in the introduction (p. 726) that Gadamer more than once directs attention to the ready oxidisability of dihydroanhydroberberine and its salts when left in contact with air (for example, *Arch. Pharm.*, 1905, **243**, 37; 1910, **248**, 671, 672, 674), and that the present author is unable to confirm this ready oxidisability. The evidence in support of the stability of dihydroanhydroberberine and its hydrochloride towards atmospheric oxygen is as follows: A specimen of dihydroanhydroberberine which had crystallised from acetone in small crystals and melted at  $167$ – $168^{\circ}$  was analysed in December, 1917, and yielded  $C=71.2$ ,  $H=5.7$ , whereas  $C_{20}H_{19}O_4N$  requires  $C=71.2$ ,  $H=5.6$  per cent. This specimen was left on a watch-glass in a large drawer which was in frequent use, fully exposed until the end of June, 1918, when it had not altered in appearance, still melted at  $167$ – $168^{\circ}$ , and yielded on analysis  $C=71.1$ ,  $H=5.6$ . In the second case, dihydroanhydroberberine hydrochloride, prepared from the pure base, was repeatedly recrystallised from dilute hydrochloric acid, and a portion taken and dried at  $90^{\circ}$ , when it yielded  $C=61.5$ ,  $H=5.7$ , whereas  $C_{20}H_{19}O_4N, HCl, H_2O$  requires  $C=61.3$ ,  $H=5.6$  per cent. The remainder (14 grams) was left on a porous plate exposed to the air, in the drawer already mentioned, for a like period of about six months, and had then the same brilliant appearance as at first. When a weighed portion was heated at  $90^{\circ}$  until constant, it lost 12.1 per cent., and the residue gave on analysis  $C=61.6$ ,  $H=5.7$ , or almost exactly the same result as before exposure. It may be pointed out that these and other analytical results point to the formula  $C_{20}H_{19}O_4N, HCl, 4H_2O$  as representing the composition of dihydroanhydroberberine hydrochloride, and show that of the  $4H_2O$ , one remains at  $90^{\circ}$ , exactly as in the case of berberinium chloride, for  $C_{20}H_{19}O_4N, HCl, 4H_2O$ , losing  $3H_2O$ , means a loss of 12.1 per cent., and the formula  $C_{20}H_{19}O_4N, HCl, H_2O$  requires  $C=61.3$ ,  $H=5.6$  per cent. Gadamer states that his analytical results point to the formula  $C_{20}H_{19}O_4N, HCl, 3H_2O$ , but

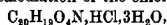
his determinations of water of crystallisation and chlorine\* agree fairly well with the formula containing  $4\text{H}_2\text{O}$ .

Since there is little difference in composition between berberinium chloride,  $\text{C}_{20}\text{H}_{18}\text{O}_4\text{NCl}$ , and dihydroanhydroberberine hydrochloride, it was still necessary to prove that the salt which had been exposed to the air consisted of the latter substance. For this purpose, the hydrochloride (13.5 grams), dissolved in a little hot water, in which it is readily soluble, was made alkaline with ammonia and allowed to remain until the viscid precipitate had hardened. While still warm, the precipitate was collected, triturated with water, and thoroughly washed; it was then dried on porous porcelain in the steam-oven, and weighed 9.75 grams, whereas the amount of dihydroanhydroberberine which should have been produced from 13.5 grams of the pure hydrochloride,  $\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}\cdot\text{HCl}\cdot 4\text{H}_2\text{O}$ , is 10.2 grams. The base on crystallisation from methyl alcohol melted at  $166\text{--}168^\circ$ , and was pure dihydroanhydroberberine. The ammoniacal mother liquors gave, on concentration under diminished pressure and admixture with a large excess of hydrochloric acid, a slight crystalline precipitate. On remaining in the ice-chest, this increased somewhat, and, after collecting, washing with dilute hydrochloric acid, and drying in the steam-oven, it weighed 0.55 gram, and consisted of berberinium chloride. Apparently, therefore, oxidation had taken place, but to a very slight degree.

*Crystallographical Examination and Comparison of Dihydroanhydroberberine and Tetrahydroanhydroberberine.*

It has already been pointed out (p. 725) that Faltis (*Monatsh.*, 1910, **31**, 565) had expressed the opinion that the base obtained by the action of concentrated alkalis on the berberinium salts is not dihydroanhydroberberine, as claimed by Gadamer (*Arch. Pharm.*, 1905, **243**, 35), but is, in fact, tetrahydroanhydroberberine. In order the more effectually to disprove this view, specially pure preparations of the substances in question were made, crystallised from acetone, and several well-developed crystals of each carefully measured.† The author is indebted to Miss Porter and Mr. T. V. Barker for undertaking the measurements.

\* There is a slip in the calculation of the chlorine content of



which should be 8.3 and not 9.5 per cent.

† Tetrahydroanhydroberberine, prepared by the reduction of berberinium chloride or sulphate with zinc and dilute acid, is rarely obtained colourless, and the crystals retain their colour persistently even after repeated recrystallisation. In order to remove the colour, a good plan is to recrystallise

*Dihydroanhydroberberine* (M. W. Porter).

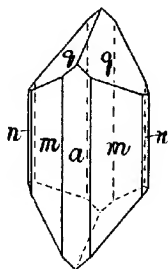
The crystals are monoclinic with the axial ratios:  $a:b:c=1.708:1.0:831$ ;  $\beta = 96^\circ 40'$ . Determinants:  $0\bar{1}\bar{1}/0\bar{1}\bar{1}/100$ . Complex symbol:  $4h;-6\frac{1}{2}/59\frac{1}{2}/-5$ . Forms observed:  $a\{100\}$ ,  $m\{110\}$ ,  $n\{120\}$ ,  $q\{011\}$ . The crystals of this compound are slender, prismatic in habit, as shown in Fig. 1. The form  $a\{100\}$  is fairly well developed, but  $m\{110\}$  predominates. The faces of the form  $n\{120\}$  are narrow. Four fairly good crystals were measured. The results of the measurements are shown below.

Face.	No. of readings.	Azimuth ( $\phi$ ).		
		Limits.	Obs.	Calc.
$a\{100\}$	7	$89^\circ 47' - 90^\circ 12'$	$89^\circ 59'$	$90^\circ 0'$
$m\{110\}$	10	$30\ 18 - 30\ 40$	$*30\ 31$	—
$n\{120\}$	9	$16\ 30 - 17\ 12$	$16\ 48$	$16\ 25$
$q\{011\}$	6	$7\ 35 - 8\ 14$	$*8\ 0$	—

Face.	No. of readings.	Polar distance ( $\rho$ ).		
		Limits.	Obs.	Calc.
$a\{100\}$	7	$90^\circ 0' - 90^\circ 8'$	$90^\circ 1'$	$90^\circ 0'$
$m\{110\}$	10	$90\ 0 - 90\ 0$	$90\ 0$	$90\ 0$
$n\{120\}$	9	$90\ 0 - 90\ 0$	$90\ 0$	$90\ 0$
$q\{011\}$	6	$39\ 51 - 40\ 6$	$*40\ 0$	—

FIG. 1.

*Tetrahydroanhydroberberine* (M. W. Porter).

The crystals are monoclinic and exhibit the forms  $o\{111\}$ ,  $c\{111\}$ ,  $a\{100\}$ , and  $c\{001\}$ , with the octahedral habit shown in Fig. 2. Crystallographic constants:  $47^\circ 54'$ ,  $a(48^\circ 17')m(41^\circ 43')b$ ,  $50^\circ 36'$ ,  $89^\circ 4'$ ; or, alternatively,  $a:b:c=1.121:1.0:904$ ,  $\beta=90^\circ 56'$ .

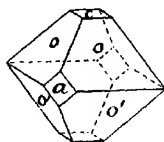
the hydrochloride from glacial acetic acid, in which it is rather sparingly soluble, until the salt is perfectly white and then to liberate the base and crystallise it from alcohol or acetone. Tetrahydroanhydroberberine purified in this way is perfectly colourless and melts at  $174^\circ$ .

Determinants: 010/001/100. Complex-symbol:  $4d; +1/59/+3$ .  
Following are the mean observations from three crystals:

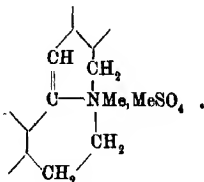
	$a$ (100).	$c$ (001).	$\sigma'$ ( $\bar{1}11$ ).	$\sigma$ (111).
Azimuth ( $\phi$ ) .....	Face of	90°0'	47°54'	*47°54'
Polar distance ( $p$ ) ...	reference	*89 4	*120 20½	58 38 (Calc. 58 37)

Although the crystals are pseudo-orthorhombic, an optical examination agreed with monoclinic symmetry.

FIG. 2.



*Dihydroanhydroberberine Methosulphate,*



This substance may be prepared by adding excess of freshly distilled methyl sulphate (10 c.c.) to a solution of dihydroanhydroberberine (10 grams) in boiling benzene, when there is no immediate precipitate, but gradually the yellow methosulphate separates in prisms. After remaining overnight, the mass is collected, washed with benzene, and dried in the steam-oven, when a yield of 10 grams is obtained, and a further crop of less pure material separates from the concentrated mother liquor. The whole is crystallised from methyl alcohol, in which the methosulphate is sparingly soluble and from which it separates in well-developed prisms. A better method of preparation is to shake the base (10 grams) with methyl sulphate (15 c.c.) in a stoppered bottle, when a thin paste is formed without development of heat. On keeping, the paste gradually becomes thicker, and after eight days combination is complete. The product is triturated with benzene, filtered, and the residue crystallised from methyl alcohol. The comparative slowness of the combination is evidenced by the fact that, if the mass after two days is washed with benzene and boiled with water, only about half dissolves as the methosulphate, and the rest is unchanged dihydro-

anhydroberberine. For analysis, the air-dried substance was dried in the steam-oven, when it lost about 8 per cent.:

0.1168 gave 0.2435  $\text{CO}_2$  and 0.0578  $\text{H}_2\text{O}$ .  $\text{C}=56.8$ ;  $\text{H}=5.5$ .

$\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4$  requires  $\text{C}=57.0$ ;  $\text{H}=5.4$  per cent.

*Dihydroanhydroberberine methosulphate* shrinks at  $140^\circ$  and melts at about  $205^\circ$  to an amber syrup; it dissolves sparingly in cold, but readily in hot water, and separates as a very voluminous mass of microscopic, lemon-yellow needles which filter with difficulty. The air-dried crystals seem to contain  $4\text{H}_2\text{O}$ , since a specimen which had been exposed to the air for ten days gave the following results:

0.1132 lost 0.0147 at  $100^\circ$ .  $\text{H}_2\text{O}=13.0$ .

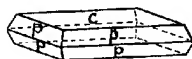
$\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4, 4\text{H}_2\text{O}$  contains  $\text{H}_2\text{O}=13.3$  per cent.

The residue, 0.0985 gave 0.2050  $\text{CO}_2$  and 0.0485  $\text{H}_2\text{O}$ .  $\text{C}=56.8$ ;  $\text{H}=5.5$  per cent.

Miss M. W. Porter was kind enough to examine some crystals of dihydroanhydroberberine methosulphate which had been obtained from methyl alcohol, and reports as follows:

The crystals are orthorhombic and exhibit the forms  $c\{001\}$  and  $p\{111\}$ . The habit is tabular, parallel to  $c$  (see Fig. 3), which is a plane of perfect cleavage. The mean results of measurement for  $p\{111\}$  are: azimuth ( $\phi$ )= $48^\circ 40'$ ; polar distance ( $\rho$ )= $64^\circ 26'$ . Axial ratios:  $a:b:c=0.879:1:1.380$ . Determinants:  $010/100/001$ . Complex-symbol:  $4d/64^\circ 26'/+3^\circ 40'$ .

FIG. 3.



The aqueous solution of the methosulphate gives no precipitate on the addition of ammonia, even on boiling, but hot concentrated sodium hydroxide produces a milky solution from which a white, crystalline precipitate separates. The methosulphate is readily soluble in glacial acetic acid, and the addition of sulphuric acid produces a pink coloration which, on keeping, becomes more intense; a drop of dilute nitric acid changes this to deep claret and then to brown. The benzene washings of the crude methosulphate, as well as the aqueous and methyl-alcoholic mother liquors, contain a second substance, which is much more readily soluble than the methosulphate and can be separated from it by fractional crystallisation from water. The amber prisms obtained in this way, on the addition of ammonia to their aqueous solution,

gave a precipitate of dihydroanhydroberberine, and consist, therefore, evidently of *dihydroanhydroberberine methyl hydrogen sulphate*:

0.1002 gave 0.2055  $\text{CO}_2$  and 0.0475  $\text{H}_2\text{O}$ .  $\text{C}=56.0$ ;  $\text{H}=5.2$ .

$\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}, \text{MeHSO}_4$  requires  $\text{C}=56.1$ ;  $\text{H}=5.1$  per cent.

When any considerable quantity of the crude mixture of methosulphate and methyl hydrogen sulphate accumulates, a good plan is to dissolve the whole in boiling water and add ammonia. The dihydroanhydroberberine which separates is rapidly collected, and is remarkably pure, whilst the hot filtrate, on keeping, deposits the pure methosulphate.

*Dihydroanhydroberberine Methiodide*,  $\text{C}_{21}\text{H}_{19}\text{O}_4\text{N}, \text{MeI}$ .—A boiling dilute solution of dihydroanhydroberberine methosulphate gives, on the addition of boiling dilute potassium iodide, a clear solution, from which the iodide immediately begins to crystallise as a lemon-yellow powder:

0.1175 gave 0.2265  $\text{CO}_2$  and 0.0472  $\text{H}_2\text{O}$ .  $\text{C}=52.6$ ;  $\text{H}=4.5$ .

$\text{C}_{21}\text{H}_{22}\text{O}_4\text{NI}$  requires  $\text{C}=52.6$ ;  $\text{H}=4.5$  per cent.

This iodide darkens rapidly above  $190^\circ$ , is brick-red at about  $200^\circ$ , and melts at about  $215$ — $220^\circ$  with effervescence to a reddish-brown froth. It is very sparingly soluble in water, but comparatively readily so in boiling alcohol, from which it separates in thin, microscopic plates. This methiodide is evidently identical with the substance which Freund and Fleischer (*Annalen*, 1915, **409**, 231) obtained from dihydroanhydroberberine by the direct action of methyl iodide, which they found to melt at  $223$ — $224^\circ$ .

The *methochloride*,  $\text{C}_{21}\text{H}_{19}\text{O}_4\text{N}, \text{MeCl}$ , was obtained by grinding the iodide to a paste with water, adding much water and freshly precipitated silver chloride, and heating on the water-bath for an hour. After filtering, the almost colourless solution was concentrated and allowed to remain, when a crust of glistening, well-developed, four-sided prisms separated, which were collected, ground, and allowed to remain exposed to the air for a week. The substance appears to contain  $5\text{H}_2\text{O}$ , of which  $4\text{H}_2\text{O}$  are removed by drying at about  $95^\circ$ :

0.1287 lost 0.0229 at  $95^\circ$ .  $\text{H}_2\text{O}=17.7$ .

$\text{C}_{21}\text{H}_{22}\text{O}_4\text{NCl}, 5\text{H}_2\text{O}$  losing  $4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=18.1$ .

After drying at  $90^\circ$ , 0.1267 gave 0.2890  $\text{CO}_2$  and 0.0671  $\text{H}_2\text{O}$ .

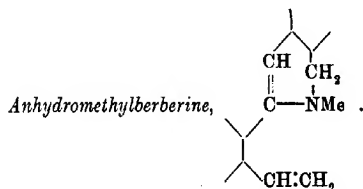
$\text{C}=61.8$ ;  $\text{H}=5.9$ .

$\text{C}_{21}\text{H}_{20}\text{O}_4\text{NCl}, \text{H}_2\text{O}$  requires  $\text{C}=62.1$ ;  $\text{H}=5.9$  per cent.

*Dihydroanhydroberberine methochloride* melts and decomposes at about  $223^\circ$  with evolution of gas to a brown syrup. It is sparingly soluble in cold, but readily so in boiling water, and a drop of the



solution mixed with dilute sulphuric acid gives, on the addition of a trace of manganese dioxide, a pink coloration which, on boiling, becomes claret coloured. It dissolves readily in hot glacial acetic acid and crystallises, on cooling, in needles. The addition of sulphuric acid to the solution of a crystal in a drop of glacial acetic acid produces an intense purple coloration. When the methochloride is heated in a drawn-out test-tube by means of a sulphuric-acid bath at  $230^{\circ}$  for a couple of minutes, methyl chloride is eliminated, and the solution of the dark brown residue in boiling methyl alcohol deposits pale brown crystals which melt at about  $165\text{--}167^{\circ}$ , and consist of dihydroanhydroberberine (compare this vol., p. 506).



Anhydromethylberberine is obtained when dihydroanhydroberberine methosulphate is digested with methyl-alcoholic potassium hydroxide, and it is important that the methosulphate should be quite free from dihydroanhydroberberine methyl hydrogen sulphate, otherwise the anhydromethylberberine will be contaminated with dihydroanhydroberberine, and then very difficult to purify. The methosulphate should therefore be recrystallised from methyl alcohol until its aqueous solution, on the addition of ammonia, remains perfectly clear, even on warming. The methosulphate (5 grams), dissolved in the least possible quantity of boiling methyl alcohol, is mixed with methyl-alcoholic potassium hydroxide (30 c.c. of 25 per cent.) and vigorously boiled, so that much of the methyl alcohol escapes. The clear solution soon clouds, and oily drops separate which sink to a yellow globule at the bottom of the vessel. After ten minutes, the whole is vigorously shaken under cold water in order to granulate the mass, water is added, the rather viscid precipitate collected, washed with water, and ground and washed with methyl alcohol, which removes a good deal of oily impurity and leaves a pale yellow, crystalline mass. Finally, the substance is rapidly crystallised from methyl alcohol or acetone. Difficulty was experienced in obtaining good analytical results until a lead chromate tube was employed:

0.1001 gave 0.2625  $\text{CO}_2$  and 0.0548  $\text{H}_2\text{O}$ . C=71.5; H=6.1.

0.1012 „ 0.2664  $\text{CO}_2$  „ 0.0551  $\text{H}_2\text{O}$ . C=71.8; H=6.1.

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}$  requires C=71.8; H=6.0 per cent.

*Anhydromethylberberine* melts at 94–95°, and, like anhydrocryptopine (m. p. 110–111°, p. 975), is sparingly soluble in methyl alcohol, from which it crystallises, if the operation is carried out rapidly and with small quantities (see below), in fern-like groups of needles; it separates from acetone, in which it is readily soluble, in pale yellow prisms. Unfortunately, these are striated, and therefore unsuitable for measurement and comparison with the crystals of anhydrocryptopine (976).

Anhydromethylberberine is a weak base, since its bright yellow solution in glacial acetic acid is precipitated by water, and it does not dissolve in very dilute hydrochloric acid in the cold.

A trace of the substance dissolved in a drop of acetic acid gives with sulphuric acid a faint yellowish-brown solution which rapidly becomes chartreuse-green, and the addition of a trace of dilute nitric acid changes the colour to bright cherry-red.

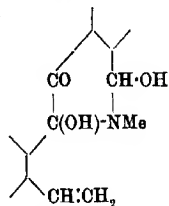
If benzenediazonium chloride is added to the solution in acetic acid, a deep orange-red coloration is produced, and precisely the same reaction is shown by anhydrocryptopine.

When boiled with methyl alcohol in contact with the air, anhydromethylberberine rapidly undergoes some profound change, since, although it is very sparingly soluble in this solvent in the cold, only a comparatively small part separates on keeping, particularly if the experiment has been carried out with large quantities of material and there is no further separation on concentrating the dark brown mother liquor. When the mother liquors from a number of crystallisations were allowed to remain in a flask exposed to the air, a crystalline crust gradually separated, and in some cases—notably when pure anhydromethylberberine had been recrystallised—the new substance separated in rosettes of garnet prisms, but the amount was always very small (990):

0.1039 gave 0.2393 CO<sub>2</sub> and 0.0511 H<sub>2</sub>O. C=62.8; H=5.4.

C<sub>21</sub>H<sub>21</sub>O<sub>7</sub>N requires C=63.1; H=5.3 per cent.

This substance, which apparently contains the grouping



and for which the name *trioxyanhydromethylberberine* is suggested, melts at 153–155° and is a very feeble base, since it does not dis-

solve in cold dilute hydrochloric acid; on boiling, decomposition appears to occur and a milky liquid is produced. The solution in glacial acetic acid is almost colourless, but becomes deep orange when mixed with sulphuric acid, and the addition of a trace of dilute nitric acid produces a dark brown coloration. The dark brown methyl-alcoholic mother liquors from which this substance had separated contained a large amount of a resinous substance, the nature of which has not been investigated.

*Reduction of Anhydromethylberberine to N-Methylisotetrahydroanhydroberberine (B).*—This reduction was carried out under the following conditions: Anhydromethylberberine, dissolved in warm concentrated hydrochloric acid or dilute sulphuric acid (20 per cent.), was immediately mixed with ice in a flat basin standing on powdered ice; a large excess of 4 per cent. sodium amalgam was then added, care being taken to keep the liquid strongly acid throughout the operation. If hydrochloric acid has been employed, the sparingly soluble hydrochloride of *N*-methylisotetrahydroanhydroberberine will have separated, and this is collected and recrystallised from much water or, better, dilute acetic acid.

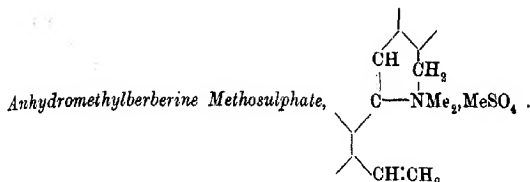
In the case of the use of sulphuric acid, which seems to lead to a rather better yield, the base is precipitated with ammonia, dissolved in dilute hydrochloric acid, and the hydrochloride recrystallised.

The pure hydrochloride is then decomposed and the base several times crystallised from methyl alcohol. (Found:  $C=71.1$ ;  $H=6.5$ .  $C_{21}H_{23}O_4N$  requires  $C=71.4$ ;  $H=6.6$  per cent.)

This substance melts at  $113-115^\circ$ , and was shown, by direct comparison, to be identical with *N*-methylisotetrahydroanhydroberberine (*B*), which Pyman (T., 1913, 103, 827, 835) obtained by the dehydration of tetrahydroanhydroberberine methohydroxide. The *hydriodide*,  $C_{21}H_{23}O_4N.HI$ , which does not appear to have been described, was prepared by adding boiling dilute potassium iodide to the boiling solution of the hydrochloride, when there was no immediate precipitate, but, on keeping, the hydriodide separated in rather indefinite balls of needles. It darkens at  $220^\circ$  and melts rather sharply at  $225^\circ$  with decomposition:

0.1005 gave 0.1938  $CO_2$  and 0.0461  $H_2O$ .  $C=52.6$ ;  $H=4.5$ .

$C_{21}H_{24}O_4NI$  requires  $C=52.4$ ;  $H=4.9$  per cent.



In preparing this substance, anhydromethylberberine (15 grams) was mixed with methyl sulphate (20 c.c.) in a bottle and well shaken, when the feebly basic nature of the substance was evidenced by the fact that there was no rise of temperature and no apparent immediate action. During twenty-four hours much had dissolved, and gradually the whole became a viscid syrup which, on further shaking, set to a semi-solid mass. After seven days, the mass was triturated with benzene, collected, washed with benzene, and left exposed until free from the solvent. It was then dissolved in boiling water, from which it separated readily in leaflets, and once it is recrystallised it becomes sparingly soluble in water. On keeping exposed to the air, the crystals lose their lustre, but the air-dry substance does not lose weight in the steam-oven, although it still appears to contain  $1\text{H}_2\text{O}$ :

0.1218 gave 0.2508  $\text{CO}_2$  and 0.0652  $\text{H}_2\text{O}$ .  $\text{C}=56.1$ ;  $\text{H}=5.9$ .

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}, \text{Me}_2\text{SO}_4, \text{H}_2\text{O}$  requires  $\text{C}=55.8$ ;  $\text{H}=5.7$  per cent.

*Anhydromethylberberine methosulphate* melts at about  $150\text{--}152^\circ$  with vigorous effervescence, due to the escape of steam, and the brown syrup, which remains, dissolves in hot water and separates on cooling in white leaflets. It crystallises from water in colourless, flat needles, and is readily soluble in boiling methyl alcohol, from which it separates in groups of thin plates. A trace of the substance dissolved in a drop of glacial acetic acid gives, with sulphuric acid, a pink solution, and a drop of dilute nitric acid, added to this changes the colour first to intense blue and then to brown.

When the solution in boiling methyl alcohol is mixed with methyl-alcoholic potassium hydroxide and heated on the steam-bath, it soon becomes milky, and an oil separates after a few minutes. The product was mixed with water, the viscid precipitate collected, washed, and dissolved in boiling methyl alcohol, from which, on rubbing with a glass rod, minute yellow prisms separated which melted at  $92\text{--}94^\circ$ , and consisted of anhydromethylberberine (979).

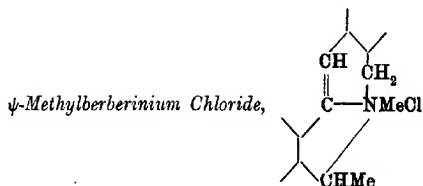
*Anhydromethylberberine Methiodide*,  $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}, \text{MeI}$ .—When

boiling dilute potassium iodide is added to the boiling dilute solution of the methosulphate, a clear solution is obtained, and remains for some time, but, on rubbing with a glass rod, the iodide immediately commences to separate in groups of flat prisms:

0.1040 gave 0.2052  $\text{CO}_2$  and 0.0461  $\text{H}_2\text{O}$ .  $\text{C}=53.7$ ;  $\text{H}=4.9$ .

$\text{C}_{22}\text{H}_{24}\text{O}_4\text{NI}$  requires  $\text{C}=53.5$ ;  $\text{H}=4.9$  per cent.

This methiodide becomes brown at  $185^\circ$  and melts at  $188\text{--}190^\circ$  with vigorous decomposition to a brown froth (980). It is comparatively readily soluble in boiling water, but sparingly so in the cold, and the hot solution, on cooling, becomes milky and then crystallises. It is rather readily soluble in boiling alcohol and separates in groups of striated plates.



This interesting substance is obtained from anhydromethylberberine methosulphate by the action of concentrated hydrochloric acid (984).

The methosulphate (1 gram), dissolved in concentrated hydrochloric acid (3 c.c.), is heated to boiling for five minutes in a sulphuric acid bath and the hydrochloric acid distilled off under diminished pressure. When the pale brown residue is dissolved in a small quantity of boiling water and stirred, crystallisation soon sets in, and the chloride separates in striated, hexagonal plates.

The ochreous mass is collected, dissolved in a little boiling water, and mixed with an equal volume of concentrated hydrochloric acid, when the chloride separates in characteristic balls of needles or plates, according to the concentration. The substance contains water of crystallisation, which was not determined, and, after drying at  $70^\circ$  and then over phosphoric oxide in a vacuum desiccator, the following analyses indicate that it still contains  $1\text{H}_2\text{O}$ :

0.1112 gave 0.2568  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C}=63.0$ ;  $\text{H}=5.9$ .

0.1118 „ 0.2562  $\text{CO}_2$  „ 0.0597  $\text{H}_2\text{O}$ .  $\text{C}=62.5$ ;  $\text{H}=5.9$ .

$\text{C}_{21}\text{H}_{22}\text{O}_4\text{NCl}\cdot\text{H}_2\text{O}$  requires  $\text{C}=62.1$ ;  $\text{H}=5.9$  per cent.

$\psi$ -Methylberberinium chloride softens at  $80\text{--}82^\circ$ , gradually shrinks, and becomes a syrup below  $100^\circ$ . It is readily soluble in warm water or methyl alcohol, but insoluble in ether, and when

ether is added to the solution in methyl alcohol, a milky liquid results, from which the chloride rapidly separates in highly characteristic stars of pale yellow needles. The solution of a trace of the chloride in a drop of acetic acid gives, on the addition of sulphuric acid, at first no coloration, but a salmon tint soon develops and rapidly changes to intense permanganate colour. A splinter of the chloride on a watch-glass, when moistened with concentrated nitric acid, dissolves to an intense crimson solution. The aqueous solution of the chloride is coloured yellow by ammonia, but gives no precipitate, and it behaves in the same way with cold sodium hydroxide, but when placed in the steam-bath the yellow solution becomes orange, then brown, and a dirty green base separates. The addition of methyl-alcoholic potassium hydroxide to the methyl-alcoholic solution of the chloride causes a separation of potassium chloride, but the yellowish-brown solution yields no precipitate with water. If the solution in dilute methyl-alcoholic potassium hydroxide is heated in the steam-bath, the liquid on the side of the test-tube dries to a brilliant crimson; after a time, this no longer occurs, and a black, amorphous precipitate separates which dissolves in hydrochloric acid to a brownish-pink solution. Even when mixed with powdered ice, the aqueous solution of the chloride instantly decolorises permanganate (984).

The *platinichloride*,  $(C_{21}H_{22}O_4N)_2PtCl_6$ , is a pale salmon coloured precipitate, and it is curious that when it is filtered off, the mother liquor is deep pink, exactly as was observed in the case of the preparation of the platinichloride from  $\psi$ -cryptopine chloride (985). When heated in a capillary tube, it loses its salmon colour at  $206^\circ$  and becomes yellow, then gradually darkens, shrinks together above  $210^\circ$ , and melts at about  $243^\circ$  with effervescence to a black tar:

0.1216 gave 0.2026  $CO_2$  and 0.0435  $H_2O$ .  $C=45.4$ ;  $H=4.0$ .

0.2124 „ 0.0366 Pt.  $Pt=17.2$ .

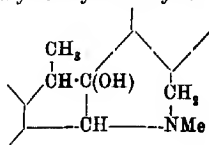
$(C_{21}H_{22}O_4N)_2PtCl_6$  requires  $C=45.3$ ;  $H=4.0$ ;  $Pt=17.5$  per cent.

*$\psi$ -Berberinium Iodide*,  $C_{21}H_{22}O_4NI$ .—The hot dilute solution of the chloride gives, with potassium iodide, a clear solution which may not crystallise for days, but gradually deposits groups of almost colourless warts:

0.1072 gave 0.2068  $CO_2$  and 0.0471  $H_2O$ .  $C=52.6$ ;  $H=4.8$ .

$C_{21}H_{22}O_4NI$  requires  $C=52.6$ ;  $H=4.6$  per cent.

This iodide darkens at  $160$ – $165^\circ$  and decomposes at  $175$ – $180^\circ$  to a brown mass. It is very sparingly soluble in water, more readily so in boiling alcohol, from which it separates in microscopic groups of needles.

*The Hydroxyisoanhydrodihydromethylberberines, (A) and (B).*

These substances, which correspond with the hydroxyisoanhydrodihydrocryptopines, (A) and (B), result from the action of dilute hydrochloric acid on anhydromethylberberine. The base (2 grams) is mixed with concentrated hydrochloric acid (2.5 c.c.) and water (8 c.c.) in a test-tube, when the crystals, although they appear to change, do not dissolve, but pass rapidly into solution on warming with the formation of a yellow liquid. The test-tube is placed in boiling water, which causes the colour to deepen considerably, and after twenty minutes the tube is withdrawn, when, in a short time, the liquid clouds and a heavy syrup separates which, on keeping, becomes a hard button.

The product may be worked up in two different ways.

(i) The whole is dissolved in hot water, made strongly alkaline with ammonia, and the chalky precipitate immediately extracted with much ether, in which, in this condition, it is readily soluble. The ethereal solution is washed, rapidly dried over anhydrous potassium carbonate, and concentrated, during which, and while the solution is still boiling, a crystalline crust of prisms begins to separate, and increases very much on keeping.\* If the ethereal solution is not too concentrated, this substance, after collecting and washing with ether, may melt at once at 208–210°, and consist of almost pure hydroxyisoanhydrodihydromethylberberine (A). If this is not the case, the substance is recrystallised from ether or from methyl alcohol.

The modification (B) of the hydroxy-compound is contained in

\* In the description of hydroxyisoanhydrodihydrocryptopine (A) (996), it is stated that attempts to obtain this base in a crystalline condition were unsuccessful. This may, however, be accomplished by employing ether as the solvent. The hydrochloride (m. p. 227°) is dissolved in hot water, the solution cooled, and covered with much pure ether; on the addition of excess of ammonia and shaking, the base passes readily into solution. The ethereal solution is dried over potassium carbonate and concentrated, when, on remaining in a closed flask for some months in the ice-chest, nodular masses separate which melt at 177–180°. (Found, C=68.0; H=6.3.  $C_{21}H_{24}O_4N$  requires C=68.3; H=6.2 per cent.) The nodules dissolve readily in boiling methyl alcohol or acetone and separate, on long keeping, in microscopic prisms.

the ethereal mother liquors, and is isolated in the manner described below.

(ii) A method of separation which allows of the modification (A) being rapidly obtained in a pure condition depends on the fact that this modification is much less readily soluble in cold methyl alcohol than the modification (B). The chalky precipitate, obtained as just described, is dried on porous porcelain, triturated with methyl alcohol, filtered, and the residue washed with methyl alcohol two or three times. After drying, the almost colourless mass melts at about  $195-197^{\circ}$ , and one recrystallisation from methyl alcohol is sufficient to raise the melting point to  $210-212^{\circ}$ , and the substance is then the pure modification (A). The methyl-alcoholic mother liquors are then mixed with water, the base extracted with ether, and the ethereal solution washed well, dried over potassium carbonate, and fractionally concentrated, when crops of crystals of varying composition are obtained, and these are comparatively easily separated into the pure modifications (A) and (B) by recrystallisation from methyl alcohol or ether.

*Hydroxyisoanhydrodihydromethylberberine* (A) is very sparingly soluble even in boiling methyl alcohol, separates in rather indefinite crusts, and melts at  $210-212^{\circ}$ . It is also sparingly soluble in boiling benzene, acetone, light petroleum, or ether, but dissolves somewhat in boiling methylal, and separates, on cooling, in warty groups:

0.1021 gave 0.2546  $\text{CO}_2$  and 0.0566  $\text{H}_2\text{O}$ . C=68.0; H=6.2.

0.1135 „ 3.8 c.c.  $\text{N}_2$  at  $16^{\circ}$  and 755 mm. N=3.8.

$\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$  requires C=68.3; H=6.2; N=3.8 per cent.

The base dissolves readily in dilute mineral acids, and as the solutions remain without crystallising, often for days, it was at first thought that the salts were very readily soluble. This is, however, not so, because in the case of the hydrochloride, for example, if a crystal of the hydrochloride (see below) is introduced into the warm, clear solution of the salt, a very sparingly soluble salt separates as a sandy, rather indefinitely crystalline powder. The characteristic behaviour of this base towards acids is well shown by rubbing a few crystals with dilute hydrochloric acid in a test-tube, when most dissolves, but some adheres to the sides as a gum. If the test-tube is placed in hot water, the gum immediately begins to crystallise, and, on stirring, the solution becomes filled with the hydrochloride, which is now remarkably sparingly soluble in boiling dilute hydrochloric acid. The base is readily soluble in acetic acid, and the addition of sulphuric acid produces a deep orange coloration.



*Hydroxyisoanhydrodihydromethylberberine (B)* separates from ethereal solution, on spontaneous concentration, in single, glistening prisms, very different in appearance from the hard crusts of the modification (A). It melts at 168—170°, and is generally more readily soluble than the modification (A). It is rather sparingly soluble in cold methyl alcohol, but readily so on warming, and separates on slow cooling in glistening prisms:

0.1032 gave 0.2589 CO<sub>2</sub> and 0.0580 H<sub>2</sub>O. C=68.4; H=6.2.

C<sub>21</sub>H<sub>23</sub>O<sub>5</sub>N requires C=68.3; H=6.2 per cent.

This base does not show the behaviour with hydrochloric acid so characteristic of the modification (A). It is readily soluble in warm dilute hydrochloric acid, and, on cooling, the solution clouds and deposits a yellow syrup which gradually hardens, but shows little tendency to crystallise.

*Action of Acetyl Chloride on the Hydroxyisoanhydrodihydromethylberberines, (A) and (B).*

The modifications (A) and (B) of this hydroxy-derivative both yield the same products when they are subjected to the action of acetyl chloride at 100°. In each case, the base (1 gram) was sealed up with freshly distilled acetyl chloride (2 c.c.), when action took place at once with some evolution of heat, and a lemon-yellow, sandy precipitate separated. After the tube had been heated in boiling water for fifteen minutes, the excess of acetyl chloride was evaporated and the residue mixed with much cold water, which caused it to become pale green. On heating to boiling, the green colour disappeared, and a viscid precipitate (C) separated, which was collected and washed with warm water. This hydrochloride dissolves in boiling methyl alcohol, and, on cooling, rhombic plates gradually separate of angle 78° which are strongly doubly refract and show straight extinction:

0.1073 gave 0.2415 CO<sub>2</sub> and 0.0562 H<sub>2</sub>O. C=61.4; H=5.8.

C<sub>22</sub>H<sub>25</sub>O<sub>6</sub>N.HCl requires C=61.6; H=5.8 per cent.

This hydrochloride melts at about 253° with vigorous decomposition to a reddish-brown froth. It dissolves in much boiling water, but is remarkably sparingly soluble in boiling dilute hydrochloric acid, and separates in groups of thin laminae with arrow-shaped ends. The hot aqueous solution yields, on the addition of ammonia, a milky liquid which soon begins to deposit colourless, crystalline flakes, and after these had been collected and washed and left to dry on porous porcelain, they were found to melt in the steam-oven and to solidify, on cooling, to a colourless resin. In contact with methyl alcohol, this resin at once became crystal-

line, dissolved on boiling, and well-developed, flat prisms separated, on keeping, which melted sharply at  $166-167^{\circ}$ :

0.1059 gave 0.2611  $\text{CO}_2$  and 0.0595  $\text{H}_2\text{O}$ .  $\text{C}=67.1$ ;  $\text{H}=6.2$ .

$\text{C}_{23}\text{H}_{26}\text{O}_6\text{N}$  requires  $\text{C}=67.2$ ;  $\text{H}=6.1$  per cent.

The methyl-alcoholic mother liquors, when left exposed to the air, deposited warty masses which melted at  $208-210^{\circ}$ , and consisted of hydroxyisoanhydrodihydromethylberberine (*A*), and it would therefore seem that the substance melting at  $165-167^{\circ}$  is the acetyl derivative of this modification (*A*). This is confirmed by the fact that this acetyl base yields, on treatment with hydrochloric acid, a very sparingly soluble hydrochloride which separates from methyl alcohol in rhombs with the angle  $78^{\circ}$ , and melts and decomposes at  $253^{\circ}$ .

The mother liquors and washings of the hydrochloride (*C*, see above) gave with ammonia a chalky precipitate, which was collected and crystallised from methyl alcohol, in which it was sparingly soluble, and from which it separated in crusts of nodules melting at  $213-215^{\circ}$  (*D*):

0.1061 gave 0.2638  $\text{CO}_2$  and 0.0593  $\text{H}_2\text{O}$ .  $\text{C}=67.8$ ;  $\text{H}=6.2$ .

$\text{C}_{23}\text{H}_{26}\text{O}_6\text{N}$  requires  $\text{C}=67.2$ ;  $\text{H}=6.1$  per cent.

This substance is presumably the acetyl derivative of hydroxyisoanhydrodihydromethylberberine (*B*). When it was mixed with warm dilute hydrochloric acid, it was converted into the hydrochloride, which separated from methyl alcohol in oblique, rhombic plates with an angle of  $70^{\circ}$ . After drying in the steam-oven until constant in weight, this salt yielded the following analysis:

0.1189 gave 0.2716  $\text{CO}_2$  and 0.0650  $\text{H}_2\text{O}$ .  $\text{C}=62.3$ ;  $\text{H}=6.0$ .

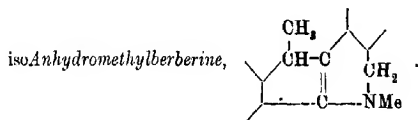
$\text{C}_{23}\text{H}_{26}\text{O}_6\text{N}, \text{HCl}$  requires  $\text{C}=61.6$ ;  $\text{H}=5.8$  per cent.

This hydrochloride darkens above  $220^{\circ}$  and decomposes at  $230^{\circ}$  with vigorous effervescence to an orange syrup. It dissolves readily in hot water and separates in a very characteristic manner, namely, in very thin, perfectly formed, nearly square plates with bevelled edges.

The mother liquors from this hydrochloride deposit, on concentration, rhombic prisms of angle  $78^{\circ}$ , which melt at  $253-255^{\circ}$  with vigorous effervescence, and evidently consist of the hydrochloride (*C*), partial molecular change having taken place during the conversion of the acetyl base (*D*) into the hydrochloride. That intramolecular changes of this nature take place readily under a variety of conditions is evidenced by the two following experiments, which were made with the object of determining whether it was possible to obtain base (*B*) from the acetyl derivative (*D*) by hydrolysis, and thus to confirm the relationship of these substances.

(i) The acetyl derivative (*D*) was boiled with dilute sulphuric acid (20 per cent.) for ten minutes, ammonia was then added, and the base crystallised from methyl alcohol, from which it separated as a rather indefinite, crystalline crust melting at 209–211°, and consisting of hydroxyisoanhydrihydroberberine (*A*). The methyl-alcoholic mother liquors deposited, on slow evaporation in the ice-chest, groups of needles which melted at 165–168°, and proved to be the modification (*B*) of the same hydroxy-base.

(ii) The acetyl derivative (*D*) was boiled with 10 per cent. methyl-alcoholic potassium hydroxide until it had dissolved and the solution concentrated, when, on keeping in the ice-chest, a crystalline substance separated which melted at 208–210°, and consisted of modification (*A*) of the hydroxy-derivative.



The hydrochloride of this base may be obtained from either of the hydroxyisoanhydrihydromethylberberines, (*A*) or (*B*), by boiling with concentrated hydrochloric acid or, better, by digesting with phosphoryl chloride. The following two experiments will illustrate this conversion.

(i) Hydroxyisoanhydrihydromethylberberine (*B*, 2 grams) was boiled with concentrated hydrochloric acid (20 c.c.) for half an hour by means of a sulphuric acid bath, during which a sparingly soluble hydrochloride separated as a crust on the sides of the test-tube. The hydrochloric acid was distilled off under diminished pressure, the pale ochreous residue dissolved in much boiling water, the solution concentrated, and left in the ice-chest, when a considerable crop of the hydrochloride of isoanhydromethylberberine gradually separated.

(ii) Hydroxyisoanhydrihydromethylberberine (*A*, 2 grams) was mixed with freshly distilled phosphoryl chloride (6 c.c.), in which it did not dissolve in the cold, but, on warming, solution took place readily with the evolution of sufficient heat to raise the temperature from 60° to the boiling point. After boiling for ten minutes, the excess of oxychloride was distilled off under 15 mm. pressure, and the deep yellow gum dissolved in much boiling water, when, on concentration and vigorous stirring, a large crop of the sparingly soluble hydrochloride of isoanhydromethylberberine separated.

The hydrochloride from either (i) or (ii) was recrystallised from much hot water, dissolved in boiling water, and mixed with ammonia, when a milky liquid resulted which soon crystallised, and the base was further purified by crystallisation from methyl alcohol:

0.1011 gave 0.2655  $\text{CO}_2$  and 0.0545  $\text{H}_2\text{O}$ .  $\text{C}=71.6$ ;  $\text{H}=6.0$ .

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}$  requires  $\text{C}=71.8$ ;  $\text{H}=6.0$  per cent.

*isoAnhydromethylberberine* melts at  $123-124^\circ$  and is readily soluble in methyl alcohol, separating in glistening prisms, which, however, were not suitable for measurement and comparison with the crystals of *isoanhydrocryptopine* (1003). It is very readily soluble in benzene, but rather sparingly so in light petroleum; it may, however, be crystallised from light petroleum (b. p.  $80-90^\circ$ ), from which it separates in groups of needles like fern fronds. It is very readily soluble in ether, and crystallises well from this solvent. It dissolves readily in acetic acid, and the addition of sulphuric acid produces a deep orange colour, which becomes brown on adding a drop of dilute nitric acid. When the base is heated in a test-tube, there is much charring and the development of a strong odour of dimethylamine.

The *Hydrochloride*,  $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}\cdot\text{HCl}$ .—This salt is sparingly soluble in water, and particularly so in dilute hydrochloric acid, and separates in brilliant, elongated prisms which are somewhat curved. It crystallises from methyl alcohol in brilliant, prismatic tablets with many facets, and melts at about  $205-210^\circ$  with previous softening.

The air-dried salt lost 3.7 per cent. at  $100^\circ$ , and gave the following results:

0.1066 gave 0.2538  $\text{CO}_2$  and 0.0556  $\text{H}_2\text{O}$ .  $\text{C}=64.9$ ;  $\text{H}=5.8$ .

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}\cdot\text{HCl}$  requires  $\text{C}=64.9$ ;  $\text{H}=5.7$  per cent.

The *Hydriodide*.—A boiling dilute aqueous solution of the hydrochloride gives no precipitate on adding boiling dilute potassium iodide, but, on keeping, the iodide soon commences to separate in indefinite, nodular groups:

0.1092 gave 0.2113  $\text{CO}_2$  and 0.0455  $\text{H}_2\text{O}$ .  $\text{C}=52.7$ ;  $\text{H}=4.6$ .

$\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}\cdot\text{HI}$  requires  $\text{C}=52.6$ ;  $\text{H}=4.6$  per cent.

When quickly heated, this hydriodide does not discolour until about  $215^\circ$ , and decomposes at about  $247^\circ$  to a nearly black froth. It is almost insoluble in cold water and sparingly so in cold alcohol, but it dissolves comparatively readily in boiling alcohol and separates in two distinct forms, namely, in stars or groups of needles or in short, brilliant prisms. When the solution is warmed,

the needles dissolve and leave the prisms, and it is evident, therefore, that this salt is dimorphic.

*Action of Dilute Sulphuric Acid on isoAnhydromethylberberine.*

The sulphate of *isoanhydromethylberberine* is readily soluble, and if the solution in a large excess of dilute sulphuric acid is boiled for half an hour and then made alkaline with ammonia, an amorphous base separates, which may be extracted with ether. The ethereal solution was thoroughly washed, dried over potassium carbonate, and concentrated, when, on remaining in the ice-chest for several days, a crust of needles formed, but in comparatively small amount. The substance was collected, washed with ether, in which it was sparingly soluble, and crystallised from methyl alcohol, in which the base is remarkably sparingly soluble, and from which it separated as a crystalline crust.

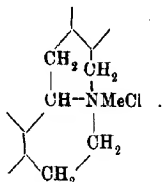
It melted at 212–215°, and consisted of hydroxy*isoanhydro*dihydroanhydro*berberine* (A). (Found: C = 68.4; H = 6.1.  $C_{21}H_{25}O_3N$  requires C = 68.3; H = 6.2 per cent.) The ethereal mother liquor from the crystallisation of this modification yielded, on concentration, a small quantity of the modification (B) melting at 165–167° (compare p. 732).

*Reduction of Dihydroanhydroberberine Methochloride.*

In studying this reduction, the methochloride (30 grams), dissolved in hot water (1 litre), was mixed with concentrated hydrochloric acid (50 c.c.) and heated to boiling in an enamelled basin. Sodium amalgam (1500 grams of 3 per cent.) was then added, in three portions, together with sufficient hydrochloric acid to keep the liquid strongly acid. The product, separated from the mercury, clouded on cooling, and when mixed with excess of ammonia deposited a viscid, pale brown precipitate which, on keeping, soon hardened. This was collected, washed with a little warm water, dried on porous porcelain, and extracted with ether (X), which left a nearly colourless mass undissolved.

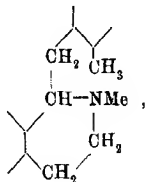
The latter was found to consist of a quaternary chloride, and a further considerable quantity of the same substance was obtained from the washings of the precipitate which had separated on the addition of ammonia. The whole was repeatedly crystallised from hot dilute hydrochloric acid, and thus separated into two quaternary chlorides, (α) and (β), melting approximately at 245–250° and 280–285° respectively. The chloride (α) is, after drying at 100°, anhydrous, and has the formula  $C_{21}H_{24}O_4NCl$ . (Found: C = 64.5; H = 6.3. Calc.: C = 64.7; H = 6.2 per cent.) The chloride (β).

melting at 280—285°, retains 1H<sub>2</sub>O after drying at 100°. (Found: C=61·7; H=6·3. C<sub>21</sub>H<sub>24</sub>O<sub>4</sub>NCl·H<sub>2</sub>O requires C=61·8; H=6·4 per cent.) There can be no doubt that these substances are the  $\alpha$ - and  $\beta$ -methochlorides of tetrahydroanhydroberberine (compare p. 733),



first described by Pyman (T., 1913, 103, 825, 826), and this was confirmed by the fact that the  $\beta$ -chloride, on digesting with methyl-alcoholic potassium hydroxide, yielded a base which separated from methyl alcohol in colourless nodules, melted at 108—110°, and consisted of methylisotetrahydroanhydroberberine (base B), which Pyman obtained by the dehydration of tetrahydroanhydroberberine methohydroxide (*loc. cit.*, p. 827). The identity was confirmed by analysis. (Found: C = 71·2; H = 6·6. C<sub>21</sub>H<sub>23</sub>O<sub>4</sub>N requires C=71·4; H=6·5 per cent.)

The ethereal extract (X) from the crude quaternary chlorides (see above) was thoroughly washed with water, dried over potassium carbonate, and evaporated, when a syrup was obtained which, even on long keeping in the ice-chest and frequent stirring, showed no signs of crystallising. That this substance is *dihydromethylisotetrahydroanhydroberberine* (p. 733),



is indicated by its properties, and an analysis supported this view and suggested that the base was nearly pure:

0·1046 gave 0·2730 CO<sub>2</sub> and 0·0672 H<sub>2</sub>O. C=71·3; H=7·1.

C<sub>21</sub>H<sub>23</sub>O<sub>4</sub>N requires C=71·0; H=7·0 per cent.

The salts are readily soluble and exhibit little tendency to crystallise. The *platinichloride* was prepared by adding platinic

chloride to a dilute solution of the hydrochloride, and is a chalky, salmon coloured precipitate:

0.1021 gave 0.1703  $\text{CO}_2$  and 0.0437  $\text{H}_2\text{O}$ .  $\text{C}=45.5$ ;  $\text{H}=4.7$ .

0.4764 „ 0.0802 Pt.  $\text{Pt}=16.9$ .

$(\text{C}_{21}\text{H}_{25}\text{O}_4\text{N})_2\text{H}_2\text{PtCl}_6$  requires  $\text{C}=45.0$ ;  $\text{H}=4.7$ ;  $\text{Pt}=17.4$  per cent.

*The Methosulphate.*—This derivative was prepared by adding methyl sulphate (3 c.c.) to the solution of the base (3 grams) in warm benzene (15 c.c.), when a rise of temperature was observed, but there was no separation even after keeping for three days in the ice-chest.

On the addition of dry ether, the methosulphate was precipitated as a syrup, and was washed with ether, dissolved in a little methyl alcohol, and boiled with a considerable excess of methyl-alcoholic potassium hydroxide for fifteen minutes under such conditions that most of the methyl alcohol distilled away. Water was added, the caseous precipitate extracted with much ether, the ethereal solution thoroughly washed, dried over potassium carbonate, and evaporated, when a syrup remained which, on keeping, gradually crystallised to a striated mass of needles.

This was dissolved in dilute hydrochloric acid, the solution filtered, made alkaline with ammonia, and again extracted with ether, the ethereal solution being dried over potassium carbonate and evaporated, when the syrup again crystallised. After remaining in contact with porous porcelain over phosphoric oxide for several days, the following results were obtained on analysis:

0.1112 gave 0.2894  $\text{CO}_2$  and 0.0735  $\text{H}_2\text{O}$ .  $\text{C}=71.0$ ;  $\text{H}=7.3$ .

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}$  requires  $\text{C}=71.5$ ;  $\text{H}=7.3$  per cent.

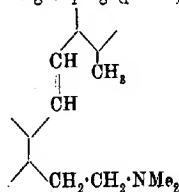
This base is very readily soluble in the usual solvents, and all attempts to recrystallise it were unsuccessful. The *platinichloride*, prepared in the usual manner, is a pale ochreous precipitate:

0.1017 gave 0.1731  $\text{CO}_2$  and 0.0449  $\text{H}_2\text{O}$ .  $\text{C}=46.4$ ;  $\text{H}=4.9$ .

0.4759 „ 0.0798 Pt.  $\text{Pt}=17.0$ .

$(\text{C}_{23}\text{H}_{27}\text{O}_4\text{N})_2\text{H}_2\text{PtCl}_6$  requires  $\text{C}=46.0$ ;  $\text{H}=4.9$ ;  $\text{Pt}=16.9$  per cent.

The analytical results and the properties of this base leave little doubt that it is *dihydrodimethylisotetrahydroanhydroberberine* (950), and contains the grouping (p. 734)

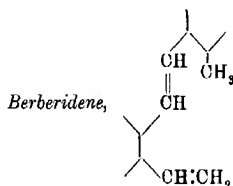


The *methosulphate* was prepared by dissolving the base (5 grams) in benzene and adding methyl sulphate (5 c.c.), when there was a considerable rise of temperature, and a syrup separated which soon commenced to crystallise and, on remaining in the ice-chest, became a soft mass of glistening needles. The crystals were collected, washed with benzene, transferred to porous porcelain, dried, and analysed:

0.1182 gave 0.2506  $\text{CO}_2$  and 0.0701  $\text{H}_2\text{O}$ .  $\text{C}=57.8$ ;  $\text{H}=6.6$ .

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}, \text{Me}_3\text{SO}_4$  requires  $\text{C}=58.2$ ;  $\text{H}=6.6$  per cent.

This methosulphate is readily soluble in water or methyl alcohol and difficult to recrystallise, but it separates, when its solution in water is allowed to concentrate over sulphuric acid, as a soft mass of needles.



In preparing this interesting substance, the methosulphate of dihydrodimehylisotetrahydroanhydroberberine was digested on the steam-bath with a large excess of methyl-alcoholic potassium hydroxide (20 per cent.), when decomposition readily set in with the elimination of trimethylamine. After twenty minutes, most of the methyl alcohol was distilled off, water was added, and the caseous precipitate extracted with much ether, in which in this condition it is moderately readily soluble. The ethereal solution was very thoroughly washed, dried over potassium carbonate, and concentrated, when, on keeping, the new substance separated as a crust of brilliant prisms:

0.1115 gave 0.3029  $\text{CO}_2$  and 0.0625  $\text{H}_2\text{O}$ .  $\text{C}=74.1$ ;  $\text{H}=6.2$ .

0.1062 „ 0.2877  $\text{CO}_2$  „ 0.0592  $\text{H}_2\text{O}$ .  $\text{C}=73.9$ ;  $\text{H}=6.2$ .

$\text{C}_{20}\text{H}_{20}\text{O}_4$  requires  $\text{C}=74.1$ ;  $\text{H}=6.2$  per cent.

Berberidene melts at  $113-114^\circ$ , and is characterised by the facility with which it crystallises. It is very sparingly soluble even in boiling methyl alcohol, and separates as a voluminous, glistening mass of irregular laminæ which, when free from any yellow mother liquor, have a most striking lilac fluorescence. It is readily soluble in benzene, but sparingly so in light petroleum, from which it separates in groups of needles. It is sparingly soluble in acetic acid in the cold, but dissolves readily on boiling,

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and separates in rhombs or in brilliant, stout prisms with an oblique termination; if, however, the separation takes place rapidly, the crystallisation may be indefinite. Berberidene exhibits a very striking difference in its behaviour with methyl and ethyl alcohols. Whilst it is very sparingly soluble in methyl alcohol and crystallises well from this solvent, it dissolves quite readily in ethyl alcohol and separates only from quite concentrated solutions, and then as an indefinite crust composed of warts.

#### *Oxidation of Berberidene.*

In studying this oxidation (p. 735), finely sieved permanganate (4 grams) was gradually added, at the ordinary temperature, to the pure substance (2.3 grams) dissolved in acetone (60 c.c.), when oxidation took place readily with distinct rise of temperature, but care was taken that this did not exceed 18°. The product was filtered, the manganese precipitate thoroughly washed with acetone (A), and repeatedly extracted with small quantities of boiling water. The brown, aqueous extract was considerably concentrated and acidified with hydrochloric acid, when a viscid, brown acid separated which proved difficult to purify, but ultimately the following process was successful: The brown mass (about 1 gram) was boiled with water (200 c.c.) and filtered from the dark brown tar; the latter was warmed with dilute ammonia, when nearly all dissolved, and, after boiling with animal charcoal and filtering, the acid was again precipitated and boiled with water (100 c.c.). The combined aqueous extracts were neutralised with sodium carbonate, mixed with a little animal charcoal, evaporated to about 20 c.c., and filtered.

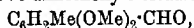
The nearly colourless filtrate gave, on acidifying, a chalky precipitate which melted at about 174°, and separated from glacial acetic acid as a satiny mass of plates. (Found: C=61.0; H=6.1.  $C_{10}H_{12}O_4$  requires C=61.2; H=6.1 per cent.)

The pure acid melted at 183–184°, and was found by direct comparison to be identical with 5:6-dimethoxy-*o*-toluic acid,  $C_9H_7Me(OMe)_2 \cdot CO_2H$ , which had been previously obtained (921) by the methylation of 5:6-dihydroxy-*o*-toluic acid. The melting point is there given as 177°, but repeated recrystallisation from glacial acetic acid raises this to 184°.

The mother liquors from the purification of the 5:6-dimethoxy-*o*-toluic acid were concentrated under diminished pressure until nearly dry, mixed with sand, and extracted with ether in a Soxhlet apparatus. The ethereal solution yielded, on evaporation, a small, crystalline residue which was separated by crystallisation from hydrochloric acid into 5:6-dimethoxy-*o*-toluic acid, and a more

readily soluble acid which separated from a little water in six-sided plates melting at about  $171-174^{\circ}$ , and, on heating, yielded an anhydride melting at about  $170-173^{\circ}$ . Since this acid gave a negative result for methoxy-groups in the Zeisel apparatus, there can be little doubt that it was hydrastic acid,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_2(\text{CO}_2\text{H})_2$ , but the quantity was insufficient for analysis. The acetone extract (A) of the manganese precipitate yielded, on evaporation, a syrup (1.2 grams) which gradually crystallised in nodular masses. When this was submitted to distillation in a current of steam, a cloudy distillate was obtained in which oily drops were visible. The whole was extracted with pure ether, the ethereal solution washed, dried over potassium carbonate, and evaporated, when a colourless oil remained which rapidly crystallised in long needles. The crystals were left in contact with porous porcelain until quite dry, melted, and, after again crystallising, transferred once more to porous porcelain. Finally, the substance was dried over phosphoric oxide in a vacuum desiccator and analysed. (Found:  $\text{C}=66.5$ ;  $\text{H}=6.8$ .  $\text{C}_{10}\text{H}_{12}\text{O}_8$  requires  $\text{C}=66.7$ ;  $\text{H}=6.7$  per cent.)

This substance was 5:6-dimethoxy-*o*-tolualdehyde,



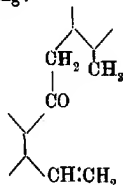
since it melted at  $52-53^{\circ}$ , and, when mixed with a specimen of this aldehyde which had previously been obtained by the methylation of 5-methoxy-*o*-tolualdehyde (915), there was no alteration in melting point.

The residue in the steam distillation flask contained a viscid oil, which was extracted with ether, the ethereal solution washed well, dried over potassium carbonate, and evaporated, when a pale yellow syrup remained, which soon began to crystallise in nodules and ultimately became solid. The mass was triturated with methyl alcohol, which removed oily impurity, transferred to porous porcelain, and recrystallised from glacial acetic acid:

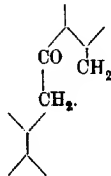
0.1265 gave 0.3285  $\text{CO}_2$  and 0.0679  $\text{H}_2\text{O}$ .  $\text{C}=70.8$ ;  $\text{H}=6.1$ .

$\text{C}_{20}\text{H}_{20}\text{O}_5$  requires  $\text{C}=70.6$ ;  $\text{H}=5.9$  per cent.

Since this substance yields a semicarbazone (see below), there can be little doubt that it is *ketodihydroberberidene* and contains the grouping:



or



G G\* 2

It is rather sparingly soluble in cold glacial acetic acid, much more readily so on boiling, and separates well in very pale yellow stars made up of elongated, rhombic plates. It melts at 118—120° and is remarkably sparingly soluble even in boiling methyl alcohol, from which it crystallises as a pale lemon-yellow powder consisting of small, glistening prisms. The crystals are coloured crimson by concentrated nitric acid, partly dissolve, and the addition of water gives an ochreous precipitate. When sulphuric acid is added to the solution of a trace of the substance in glacial acetic acid, a brown coloration is obtained, which is intensified by the addition of a drop of dilute nitric acid.

The *semicarbazone*,  $C_{21}H_{23}O_5N_3$ , was prepared by boiling the substance with much alcohol and excess of semicarbazide hydrochloride and sodium acetate, when solution took place readily, and, on evaporation to dryness, a crystalline mass remained. This was triturated with water, collected, washed well, and crystallised from methyl alcohol:

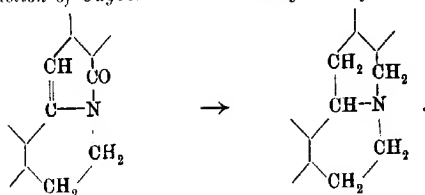
0.1027 gave 0.2376  $CO_2$  and 0.0570  $H_2O$ .  $C=63.1$ ;  $H=6.1$ .

0.1239 „ 9.7 c.c.  $N_2$  at 17° and 752 mm.  $N=10.6$ .

$C_{21}H_{23}O_5N_3$  requires  $C=63.5$ ;  $H=5.8$ ;  $N=10.6$  per cent.

This *semicarbazone* melts and effervesces at about 218—220° and is sparingly soluble in boiling methyl alcohol, from which it separates in nodular masses.

*Reduction of Oxyberberine to Tetrahydrooxyberberine,*



The main difficulty in carrying out this reduction is the sparing solubility of oxyberberine in dilute acids or in organic solvents, but ultimately the following conditions were found to give the desired result.\* Oxyberberine (10 grams), suspended in alcohol (260 c.c. of 97 per cent.), is gradually mixed with sulphuric acid (130 c.c. of 97 per cent.), when the heat generated brings about complete solution and there is no separation of oxyberberine on keeping. The electrolytic cell consisted of a glass jar 20 cm. high

\* I am indebted to Mr. G. R. Clemo for assistance in carrying out this reduction.

and of 1 litre capacity; the cathode was a sheet of lead which just fitted round the inside of the glass jar, and, previous to the experiment, had been coated with a layer of electrolytic lead. The anode was a strip of lead, and this was placed in a porous cell, 5 cm. in diameter, containing dilute sulphuric acid (20 per cent.), which was replenished from time to time during the experiment. In carrying out the reduction, the solution, prepared as described above, was placed in the cathodic compartment and a current of about 6 amperes passed for forty-eight hours. The pale yellow product was mixed with ice and water (about 500 grams), allowed to remain for twenty-four hours, and then filtered. The rather considerable grey precipitate (5.3 grams) is largely soluble in hot glacial acetic acid, and, after filtering, the solution deposits oxyberberine acetate (1.5 grams). The portion insoluble in acetic acid (0.8 gram) melts above  $300^{\circ}$ , and was not further examined. The filtrate from the grey precipitate gives with excess of ammonia a dark-coloured precipitate (4.6 grams), which is collected, dried, and digested with a little methyl alcohol, when much of the dark impurity dissolves and a much cleaner product is left. This is dissolved in boiling, very dilute hydrochloric acid with the addition of animal charcoal and concentrated, when, on keeping, a deep ochreous, crystalline precipitate separates in quantity. The hydrochloride is collected, recrystallised from boiling glacial acetic acid, and the colourless salt decomposed by ammonia. Finally, the base is twice crystallised from acetone, from which it separates in colourless, glistening leaflets. (Found: C = 70.6; H = 6.2.  $C_{20}H_{21}O_4N$  requires C = 70.8; H = 6.2 per cent.)

This substance melted at  $170$ — $171^{\circ}$ , and a careful examination both of the base and of its salts clearly established the identity with tetrahydroanhydroberberine (m. p.  $170$ — $171^{\circ}$ ). Moreover, a mixture of the substance with tetrahydroanhydroberberine melted at  $170$ — $171^{\circ}$ .

The author is much indebted to Mr. Fred Hall for carrying out the analyses given in this paper.

THE UNIVERSITY CHEMICAL LABORATORIES,  
OXFORD.

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LXVI.—*Morindone.*

By JOHN LIONEL SIMONSEN.

DURING the past few years, owing to the shortage of synthetic dyes, the use of natural colouring matters has, to some extent, been revived, and it appeared, therefore, to be a matter of some interest to attempt to elucidate the constitution of the main constituent of *Morinda citrifolia* and *M. umbellata*, morindone, since the root bark of this tree at one time found considerable application in India for the dyeing of cloth.

Morindone occurs in the root bark mainly in the form of the glucoside, morindin, although a small quantity of the free colouring matter is present in the bark. Morindin appears to have been first isolated from *M. citrifolia* by Anderson (*Annalen*, 1849, 71, 216). He ascribed to it the formula  $C_{23}H_{30}O_{15}$ , and by sublimation obtained a substance resembling alizarin in its properties, to which he gave the name morindone. Subsequent investigators appear to have regarded morindin as identical with ruberythric acid and morindone as identical with alizarin. Thorpe and Greenall (T., 1887, 51, 52), and later Thorpe and Smith (T., 1888, 53, 171), using *M. citrifolia* as the source of their material, proved conclusively, however, that morindone possessed the formula  $C_{17}H_{10}O_8$ , and were of the opinion that morindin was more correctly represented by the formula  $C_{26}H_{28}O_{14}$  than by the formula suggested by Anderson. They further considered morindone to be a trihydroxymethylanthraquinone.

The presence of morindin and morindone in *M. umbellata* was first proved by Perkin and Hummel (T., 1894, 65, 851) in their investigation of the constituents of the root bark of this tree. They confirmed the formula  $C_{26}H_{28}O_{14}$  (with eight hydroxy-groups) for morindin, and they further showed that in all probability morindone was a trihydroxymethylanthraquinone derived from 2-methylanthraquinone, since, when distilled with zinc dust, 2-methylanthracene was obtained.

Subsequently, Oesterle and Tisza (*Arch. Pharm.*, 1907, 245, 534) investigated once more the constituents of *M. citrifolia*. They drew the conclusion that morindin from that source had the formula  $C_{27}H_{30}O_{15}$  and contained nine hydroxy-groups. They based this conclusion on an analysis of morindin, its acetyl and benzoyl derivatives, and on a quantitative determination of the products of hydrolysis. The properties of the morindin obtained by these authors, and also those of its derivatives, are at distinct

variance with those described by Perkin and Hummel (*loc. cit.*). Perkin (P., 1908, 24, 150) directed attention to these discrepancies and published further analyses in support of his formula for morindin from *M. umbellata*, and suggested that the morindin derived from *M. umbellata* and *M. citrifolia* might be different.

With regard to the constitution of morindone, beyond the fact that it possesses the formula  $C_{15}H_{10}O_5$ , contains three hydroxy-groups, and yields 2-methylantracene on distillation with zinc dust, little is known. Perkin (Thorpe's "Dictionary of Applied Chemistry," III, 547) has suggested either that morindone might be a methylantragallol or that it might contain a  $-CH_2OH$  group, the presence of such a group having been suggested by Robinson and Simonsen (T., 1909, 95, 1088) to explain the relationship between aloe-emodin and rhein, since, as he pointed out, the colour reactions of morindone are somewhat remarkable.

For the preparation of the morindin and morindone required for the experiments described in this paper, the author has used the root bark of *M. citrifolia*, which was obtained for him by Dr. J. R. Henderson, of the Madras Museum, and Mr. Y. Narasimhan, lecturer in chemistry, Maharaja's College, Vizianagram, and a considerable quantity of the bark was very kindly extracted for him by Drs. Fowler and Watson at the Indian Institute of Science, Bangalore. The author wishes to take this opportunity of expressing his thanks to these gentlemen.

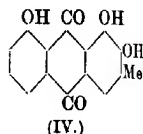
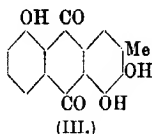
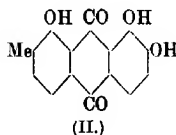
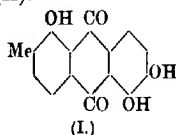
The morindin was extracted and purified essentially by the methods used by Perkin and Hummel, and it is not necessary to describe them in detail. In view of the discrepancies between the work of Perkin and Hummel and that of Oesterle and Tisza mentioned above, a specimen of morindin was very carefully purified by repeated crystallisation from 75 per cent. alcohol, when it was obtained in voluminous, yellow needles which, when rapidly heated, melted at  $250-251^\circ$ ; when slowly heated, it sintered at  $235^\circ$  and melted at  $245^\circ$ . (Oesterle and Tisza state that it commenced to sublime at  $235^\circ$  and melted at  $245^\circ$ . Perkin and Hummel do not give a melting point.) The analytical data agreed well with the formula  $C_{26}H_{28}O_{14}$  suggested by Perkin. The acetyl derivative was also prepared, and was found to melt at  $239-240^\circ$ . (Oesterle and Tisza give  $236^\circ$ , Perkin  $246-248^\circ$ .) As stated by Perkin, it is very sparingly soluble in cold alcohol, somewhat more readily so in the hot solvent, and contains eight acetyl groups. There would therefore appear to be no difference between the morindin derived from *M. citrifolia* and *M. umbellata*, and the discrepancies between the results of Perkin and Hummel and those of Oesterle and Tisza must be ascribed to some other cause. The author had

hoped to make a direct comparison of the morindins obtained from these two sources, but up to the present he has not succeeded in obtaining a specimen of the root bark of *M. umbellata*.

Attempts to isolate in a pure state the sugar formed by the hydrolysis of morindin were unsuccessful. The phenylosazone was prepared, but was found to be a mixture.

*The Constitution of Morindone.*

From a consideration of the experiments described in this paper and from the results obtained by previous investigators, the author would suggest that morindone is best represented either as a hydroxymethylanthrarufin (I) or as a hydroxymethylchrysin (II).



The evidence in support of this view may, perhaps, best be summarised as follows:

(i) The methyl group is in position 2, since morindone on distillation with zinc dust yielded 2-methylantracene (Perkin and Hummel, *loc. cit.*, p. 856).

(ii) Morindone contains three hydroxy-groups, since it yields triacetyl, tribenzoyl, and trimethoxy-derivatives.

(iii) Two of the hydroxy-groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yielded a monomethyl ether (see p. 773).

(iv) Morindone is a mordant dye resembling alizarin, and hence probably has two of the hydroxy-groups in the 1:2-position.

(v) The hydroxy-group, which undergoes methylation with methyl iodide, must be present in the same ring as another hydroxy-group, since *morindone monomethyl ether* is completely destroyed when oxidised with an alkaline solution of potassium permanganate, only oxalic acid being isolated from the products (see p. 773).

(vi) Morindone cannot be a derivative of anthragallol or purpurin, since it is perfectly stable in alkaline solution and does not undergo oxidation even when air is drawn through such a solution for several days.

(vii) The presence of a  $\cdot\text{CH}_2\cdot\text{OH}$  group, as suggested by Perkin, is unlikely, since all attempts to detect such an alcoholic grouping by oxidation or displacement of the hydroxy-group by a halogen were unsuccessful.

From the above, it follows that the only positions for the hydroxy-groups are as in 1:5:6-trihydroxyanthraquinone or 1:7:8-trihydroxyanthraquinone.

(viii) It is suggested that the methyl group must be in the ortho-position with respect to one of the hydroxy-groups, since all attempts to oxidise it to a carboxyl group by means of chromic acid have proved unsuccessful, the molecule being completely destroyed when once attacked by the oxidising agent. As is well known, *o*-xylene cannot be oxidised to phthalic acid by means of chromic acid, and the author has further found that whereas *p*-tolyl methyl ether when oxidised by means of chromic acid in acetic acid solution gave an excellent yield of anisic acid, *o*-tolyl methyl ether under similar conditions did not yield a trace of the corresponding *o*-methoxy-acid.

(ix) If the view be accepted that the methyl group is in the ortho-position with respect to one of the hydroxy-groups, then four formulæ derived from hydroxyanthrarufin or hydroxychrysazin become possible (I, II, III, and IV). The author would reject formulæ III and IV, since it is highly improbable that substances possessing these formulæ would be methylated by methyl iodide, owing to steric hindrance.

(x) In deciding between formulæ I and II, it would appear that formula I is the more probable, since in its colour reactions morindone resembles more closely hydroxyanthrarufin than hydroxychrysazin. Hydroxyanthrarufin dissolves in sulphuric acid with a violet colour which, on the addition of boric acid, becomes blue; morindone dissolves in sulphuric acid with a blue colour, which is not changed on the addition of boric acid; moreover, the sulphuric-boric acid solutions of hydroxyanthrarufin and morindone are practically indistinguishable in colour. Hydroxychrysazin, on the other hand, dissolves in sulphuric acid with a red colour, which becomes purple on the addition of boric acid. The bluer shades exhibited by morindone are explained by the presence of the methyl group, since, as is well known, methylalizarin yields bluer shades than does alizarin.

Many experiments were made with the object of confirming the



formula suggested above for morindone, but up to the present without success. Morindone trimethyl ether was found to be extremely resistant to oxidising agents. It was only slowly attacked by an alkaline solution of potassium permanganate even in boiling solution. Experiments involving the use of either chromic acid or nitric acid gave only negative results.

The synthesis of morindone is being attempted, but the problem seems to be a difficult one.

#### EXPERIMENTAL.

##### *Morindin.*

The material, isolated and crystallised as described on p. 767 (Found: C=55.3; H=4.9.  $C_{26}H_{28}O_{14}$  requires C=55.3; H=4.9 per cent.), was hydrolysed with an alcoholic solution of sulphuric acid, when 0.7556 gave 0.3632 morindone. Yield of morindone=48.1 per cent., whereas if the formula for morindin were  $C_{26}H_{28}O_{16}$ , the yield of morindone should be 48.0 per cent.

*Acetylmorindin.*—This substance was readily prepared by boiling morindin with acetic anhydride containing a trace of pyridine for two hours. It separated from dilute acetic acid in pale sulphur-yellow needles, which melted at 239–240°. For analysis it was dried at 120° (Found: C=56.1; H=5.1.  $C_{42}H_{44}O_{22}$  requires C=56.0; H=4.9 per cent.). The number of acetyl groups present was determined by A. G. Perkin's method, and was found to be eight. 0.2074 gave 0.1103  $C_2H_4O_2$ , whence Ac=38.2, whereas this amount of a substance of the formula  $C_{26}H_{28}O_{14}(Ac)_8$  should yield 0.1106  $C_2H_4O_2$ , Ac=38.2 per cent.\*

##### *Morindone.*

The morindone required for these experiments was obtained from morindin by hydrolysis with an alcoholic solution of sulphuric acid. After crystallisation from toluene, it melted at 275°, and showed all the properties ascribed to this substance (Found: C=66.4; H=3.7. Calc.: C=66.7; H=3.7 per cent.). Morindone was not attacked when heated with an acetic acid solution of hydrogen bromide (saturated at 0°) for some hours at 100° in a sealed tube, nor was it found to be altered when air was drawn through an alkaline solution for some days.

*Acetylmorindone.*—Acetylmorindone was prepared by heating morindone for two hours with acetic anhydride and anhydrous

\* Oesterle and Tisza's formula  $C_{27}H_{21}O_{14}(Ac)_8$  requires Ac=39.8 per cent.

sodium acetate. It was purified by crystallisation from acetic acid, when it was obtained in pale yellow needles melting at  $249^{\circ}$  and commencing to sinter slightly at  $243^{\circ}$ . This melting point is considerably higher than that given by Perkin and Hummel (*loc. cit.*, p. 856), who state that acetylmorindone melts at  $222^{\circ}$ . I am, however, informed by Prof. Perkin that this value for the melting point is probably due to a misprint.

For analysis, a specimen was dried at  $120^{\circ}$ :

0.1129 gave 0.2645  $\text{CO}_2$  and 0.0427  $\text{H}_2\text{O}$ .  $\text{C}=63.8$ ;  $\text{H}=4.2$ .

$\text{C}_{21}\text{H}_{16}\text{O}_8$  requires  $\text{C}=63.6$ ;  $\text{H}=4.0$  per cent.

Acetylmorindone was not readily attacked by chromic acid, and all attempts to oxidise the methyl group by this reagent were unsuccessful. Thus, when treated with the quantity of chromic acid calculated to oxidise the methyl group to a carboxyl group, a portion of the substance appeared to undergo complete destruction, the remainder being unattacked. A careful examination of the chromic acid solution failed to reveal the presence of any derivative of phthalic acid. When treated with an acetic acid solution of hydrogen bromide (saturated at  $0^{\circ}$ ) in a sealed tube at  $100^{\circ}$ , hydrolysis of the acetyl derivative took place, but no trace of a halogen derivative was formed, as would in all probability have been the case if a  $\text{-CH}_2\text{-OAc}$  group had been present (compare Perkin and Simonsen, T., 1904, 85, 854; Müller, T., 1907, 91, 1782).

*Benzoylmorindone.*—Morindone (1 gram) was mixed with pyridine (5 c.c.), and, after cooling in ice, benzoyl chloride (2 grams) was gradually added. The reaction proceeded readily, and, after remaining for thirty minutes, the mixture was poured into water, when a viscid oil separated, which rapidly solidified on triturating with hot alcohol. It was crystallised from acetic acid, when it was obtained in nodules of fine, yellow needles melting at  $218\text{--}219^{\circ}$ . For analysis, it was dried at  $120^{\circ}$ :

0.1079 gave 0.2924  $\text{CO}_2$  and 0.0403  $\text{H}_2\text{O}$ .  $\text{C}=73.9$ ;  $\text{H}=4.1$ .

$\text{C}_{30}\text{H}_{22}\text{O}_8$  requires  $\text{C}=74.2$ ;  $\text{H}=3.8$  per cent.

*Methylation of Morindone: Morindone Monomethyl Ether and Trimethyl Ether.*

Many experiments were made with a view to devise a satisfactory method for the preparation of morindone trimethyl ether. It was ultimately found that the following somewhat laborious process gave the best results.

Morindone (3 grams) was mixed with a solution of potassium

hydroxide (12 grams) dissolved in water (15 c.c.) and treated with methyl sulphate (15 c.c.), which was added all at once. The mixture was vigorously stirred, and when the reaction was complete, the same quantities of alkali and methyl sulphate were added. The alkaline solution, which was now deep red, was boiled, acidified, the crude methylation product collected, and again treated with alkali and methyl sulphate as before. The red solution contained in suspension a deep red, sparingly soluble potassium salt and the yellow trimethyl ether. It was filtered through cloth, and the residue boiled with dilute alkali and filtered, this treatment being repeated three times, when the filtrate should only be slightly red. The residue was ground with a considerable volume of chloroform, which dissolved the morindone trimethyl ether, leaving the insoluble, red potassium salt of the monomethyl ether *A* (see p. 773). The chloroform extract was evaporated, the crude, pale yellow trimethyl ether dissolved in hot toluene, and the toluene solution repeatedly washed with hot dilute alkali, which removed a further quantity of partly methylated morindone. (The alkaline washings were mixed with *A*.)

After separating from the alkali, the toluene solution was filtered, the toluene removed in a current of steam, when the nearly pure trimethyl ether was obtained. It was crystallised from acetic acid, when it separated in pale yellow needles melting at  $229^{\circ}$ , as stated by Oesterle and Tisza:

0.1013 gave 0.2566  $\text{CO}_2$  and 0.0426  $\text{H}_2\text{O}$ .  $\text{C}=69.1$ ;  $\text{H}=4.7$ .

$\text{C}_{18}\text{H}_{16}\text{O}_5$  requires  $\text{C}=69.2$ ;  $\text{H}=5.1$  per cent.

Morindone trimethyl ether, when pure, is insoluble in alkali; in sulphuric acid it dissolves to a deep blue solution.

The oxidation of morindone trimethyl ether has been carefully investigated. The ether was found to be extremely stable to chromic acid, and the greater part was recovered unchanged when oxidised with the equivalent quantity of oxidising agent, the remainder being apparently completely destroyed. When suspended in dilute sodium carbonate solution and boiled with a solution of potassium permanganate for several days, it was slowly oxidised. Much of the ether remained unattacked, and, with the exception of oxalic acid, no acid could be isolated in sufficient quantity for identification. When nitric acid was used as the oxidising agent, only oxalic acid appeared to be formed.

The sparingly soluble red potassium salt *A*, mentioned above, was suspended in hot water, decomposed with hydrochloric acid, and the brown solid which separated was collected. It was purified

by repeated crystallisation from acetic acid. For analysis, it was dried at 120°:

0.1012 gave 0.251  $\text{CO}_2$  and 0.0388  $\text{H}_2\text{O}$ . C=67.6; H=4.2.

0.1028 „ 0.2561  $\text{CO}_2$  „ 0.038  $\text{H}_2\text{O}$ . C=67.9; H=4.1.

$\text{C}_{16}\text{H}_{12}\text{O}_8$  requires C=67.6; H=4.2 per cent.

*Morindone monomethyl ether* crystallises in iridescent, brown needles melting at 248°. It is readily soluble in chloroform, toluene, or hot acetic acid, more sparingly so in ether or ethyl acetate, and very sparingly so in alcohol. It dissolves in concentrated sulphuric acid with a colour similar to that shown by morindone, only slightly redder. The sulphuric acid solution on the addition of a crystal of potassium nitrate gives a fine, greenish-red coloration. In fuming nitric acid, it dissolves with a transient red colour, yielding almost immediately a reddish-brown solution. It forms sparingly soluble red sodium and potassium salts, the solutions of which exhibited a slight fluorescence reminiscent of eosin. An attempt was made to determine the number of methoxy-groups present by the ordinary Zeisel method, but owing to the sparing solubility of the substance, the results were always low, although the heating was continued for from four to five hours and the hydriodic acid was mixed with acetic anhydride. Morindone monomethyl ether is readily attacked by an alkaline solution of potassium permanganate; it appears to undergo complete disintegration, and the bearing of this fact on the determination of the constitution of morindone has already been discussed.

Morindone monomethyl ether was also prepared by treating morindone with methyl iodide in the presence of sodium methoxide. Morindone (0.5 gram) was mixed with sodium methoxide (1.3 grams of sodium), and, after the addition of methyl iodide (0.8 gram), the mixture was heated in a sealed tube at 100° for eight hours. The deeply coloured product was poured into water, and, after the addition of potassium hydroxide solution, was boiled, filtered, and the residual potassium salt well washed with hot dilute alkali until the washings were only faintly coloured. The salt was decomposed with dilute hydrochloric acid, and the brown solid thus obtained (0.1 gram) was collected and recrystallised from acetic acid, when it melted at 247–248° and showed all the properties of morindone monomethyl ether. The melting point was not altered on admixture with an equal amount of the monomethyl ether prepared by means of methyl sulphate, as described above.

*Diacylmorindone Monomethyl Ether*.—This substance was

readily prepared when the monomethyl ether was heated for two hours with acetic anhydride and anhydrous sodium acetate. It was crystallised from acetic acid and dried at  $120^{\circ}$  for analysis:

0.1042 gave 0.2494  $\text{CO}_2$  and 0.041  $\text{H}_2\text{O}$ .  $\text{C}=65.3$ ;  $\text{H}=4.3$ .

$\text{C}_{20}\text{H}_{18}\text{O}_7$  requires  $\text{C}=65.2$ ;  $\text{H}=4.3$  per cent.

*Diacetylmorindone monomethyl ether* separates from acetic acid in yellow, hexagonal prisms melting at  $245-246^{\circ}$ . It is sparingly soluble in hot alcohol.

#### *The Sugars from Morindin.*

In one experiment, the acid mother liquor from which the morindone had been separated was treated with sodium acetate until the excess of mineral acid was neutralised, and the solution concentrated to a small bulk. Excess of phenylhydrazine was added, and, after heating on the water-bath for one hour, the brownish-yellow osazone was collected. After repeated fractional crystallisation from alcohol, a sparingly soluble fraction was obtained which separated in fine yellow needles decomposing at  $207^{\circ}$ :

0.0689 gave 11 c.c.  $\text{N}_2$  at  $30^{\circ}$  and 760 mm.  $\text{N}=17.2$ .

$\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}_4$  requires  $\text{N}=17.1$  per cent.

This substance would, therefore, appear to be the osazone of a pentose, and is possibly identical with the osazone (m. p.  $202-203^{\circ}$ ) described by Perkin (*loc. cit.*, p. 150), but owing to the small quantity of material which was obtained in a pure state, great trust cannot be placed in the result of the analysis. From the mother liquor from which the above-mentioned osazone had been separated, a small quantity of another osazone was isolated, in stout yellow needles, which melted at about  $195^{\circ}$  and were readily soluble in alcohol.

The author wishes to thank Mr. M. Gopala Rau, M.A., for the care with which he made the analyses required for this and the following communication.

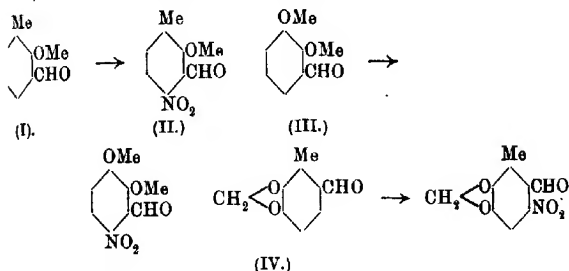
THE PRESIDENCY COLLEGE,  
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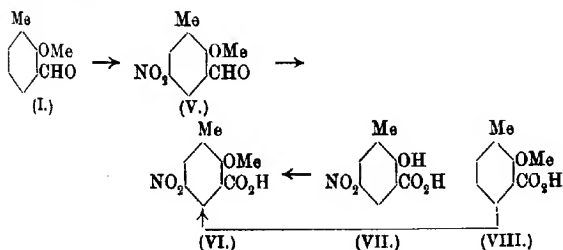
LXVII.—*The Nitration of 2- and 6-Methoxy-m-Tolualdehydes and m-Toluic Acids.*

By JOHN LIONEL SIMONSEN.

FOR synthetical experiments in the anthraquinone group, the author was desirous of preparing 3-methoxy-4-methylphthalic acid, and it appeared probable that the simplest method would be by nitrating 2-methoxy-m-tolualdehyde (I), when it was expected that the nitro-group would enter the ortho-position with respect to the aldehyde group with the formation of 4-nitro-2-methoxy-m-tolualdehyde (II), which could then be readily converted into the required acid, for it has been shown that *o*-veratraldehyde (III) and 5:6-methylenedioxy-*o*-tolualdehyde (IV), on nitration, yield nitro-derivatives containing the nitro-group in the ortho-position with respect to the aldehyde group (Perkin and Robinson, T., 914, 105, 2389; Perkin, T., 1916, 109, 910).

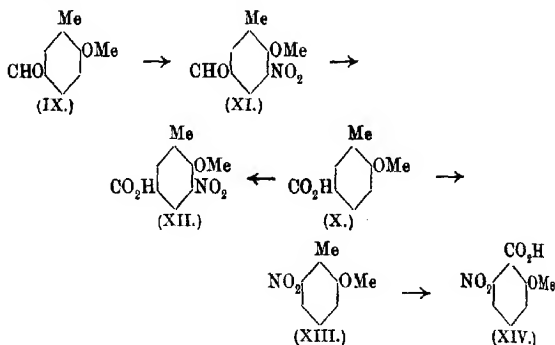


This expectation was not, however, realised, for when 2-methoxy-m-tolualdehyde was treated with nitric acid under the conditions described in the experimental part of this paper (see p. 778), an almost quantitative yield of 5-nitro-2-methoxy-m-tolualdehyde (V) was obtained.



The constitution of this aldehyde was readily proved by the fact that on oxidation it was converted into 5-nitro-2-methoxy-*m*-toluic acid (VI), an acid which was readily obtained by the methylation of 5-nitro-2-hydroxy-*m*-toluic acid (VII) (Einhorn and Pfl., *Annalen*, 1900, 311, 47; Fortner, *Monatsh.*, 1901, 22, 939).

5-Nitro-2-methoxy-*m*-toluic acid was also prepared by the nitration of 2-methoxy-*m*-toluic acid (VIII), which was obtained by the oxidation of the aldehyde.



During the preparation of the 2-hydroxy-aldehyde, a considerable quantity of the 6-hydroxy-aldehyde was obtained, and it appeared, therefore, to be of some interest to investigate the nitration of 6-methoxy-*m*-tolualdehyde (IX) and 6-methoxy-*m*-toluic acid (X). The aldehyde on nitration gave an excellent yield of the 5-nitro-derivative (XI), the constitution of which was proved by the fact that on treatment with acetone and alkali it yielded the corresponding derivative of distyryl ketone, no formation of indigotin taking place, which would have been the case if the nitro-group had entered either of the positions ortho to the aldehyde group. The nitro-aldehyde yielded on oxidation the corresponding acid (XII), which acid was also formed by the nitration of 6-methoxy-*m*-toluic acid.

At the same time, there was obtained a considerable quantity of a neutral substance melting at 69°, which would appear to be 6-nitro-*o*-tolyl methyl ether (XIII). As was to be expected of a substance possessing this constitution, some difficulty was experienced in converting the methyl group into a carboxyl group. This was ultimately accomplished by oxidation with chromic acid in concentrated sulphuric acid solution, when an acid was obtained crystallising in prismatic needles and melting at 161°. Simonsen and

Rau (T., 1916, 111, 223 *et seq.*) have described three of the four possible isomeric nitro-2-methoxybenzoic acids; this acid was found not to be identical with any of the three, and it is in all probability 6-nitro-2-methoxybenzoic acid (XIV). Unfortunately, it was not obtained in sufficient quantity for a detailed examination to be made.

The results described above are of some interest in illustrating the difference in orientating effect of methyl and methoxy-groups. It has been suggested (Simonsen and Rau, *loc. cit.*) that a negative group in the ortho-position with respect to a positive group tends to neutralise such a grouping, and the orientating effect is then in the main exercised by the remaining positive group in the molecule. Whilst this appears to be the case in the nitration of acetyl-amino-methoxy-derivatives and also of other methoxy-derivatives, the rule is evidently not of any general application.

#### EXPERIMENTAL.

##### 2-Methoxy-m-tolualdehyde (I).

The phenolic aldehyde (10 grams) was dissolved in sodium methoxide (2 grams of sodium) and treated with methyl sulphate (15 grams), the addition of the same quantities of alkali and methyl sulphate being repeated three times. The solution was then heated on the water-bath for fifteen minutes to complete the decomposition of the methyl sulphate, water added, the methoxy-aldehyde extracted with ether, and the ethereal solution dried and evaporated.

2-Methoxy-m-tolualdehyde was obtained as a viscid, pleasant-smelling oil which boiled at about 120°/6 mm. With concentrated sulphuric acid it gave a cherry-red coloration.

The oxime was best prepared by dissolving the aldehyde (1.3 grams) in alcohol, and, after the addition of hydroxylamine hydrochloride (2 grams) and sodium acetate (2 grams), the mixture was heated on the water-bath for half an hour. On pouring into water, the oxime separated in silky needles, which were purified by crystallisation from methyl alcohol. It melted at 118°:

0.1558 gave 12.9 c.c.  $N_2$  at 33° and 759 mm.  $N=8.7$ .

$C_9H_{11}O_2N$  requires  $N=8.5$  per cent.

The semicarbazone, prepared in the usual manner, crystallised from alcohol, in which it was somewhat sparingly soluble, in white, microscopic needles melting at 224°:

0.0906 gave 16.8 c.c.  $N_2$  at 30° and 760 mm.  $N=20.0$ .

$C_{10}H_{13}O_2N_3$  requires  $N=20.2$  per cent.



*Nitration of 2-Methoxy-m-tolualdehyde. 5-Nitro-2-methoxy-m-tolualdehyde (V).*

In one experiment, the aldehyde (2 grams) was added gradually to nitric acid (D 1.52:10 grams), which was kept well cooled in ice. The reaction proceeded smoothly, and, after remaining for fifteen minutes, the mixture was poured on ice, when an oil separated which rapidly solidified. This was collected, triturated with dilute sodium carbonate solution\* to remove a trace of acid, dried on porous porcelain, and purified by crystallisation from a mixture of ether and light petroleum (yield, 2.2 grams):

0.1634 gave 10.7 c.c.  $N_2$  at 30° and 759 mm.  $N=7.0$ .

$C_9H_9O_4N$  requires  $N=7.2$  per cent.

5-Nitro-2-methoxy-m-tolualdehyde crystallises in balls of needles melting at 61—62°. It is readily soluble in the ordinary organic solvents with the exception of light petroleum, in which it is somewhat sparingly soluble. The 5-nitro-aldehyde was found to be the sole product of the reaction, since no trace of an isomeride could be isolated from the mother liquors.

The semicarbazone crystallised from alcohol in fine, woolly needles which decomposed at 233°:

0.0948 gave 19.4 c.c.  $N_2$  at 32° and 758 mm.  $N=22.0$ .

$C_{10}H_{12}O_4N_4$  requires  $N=22.2$  per cent.

*5:5'-Dinitro-2:2'-dimethoxydi-3-m-methylstyryl Ketone,*  
 $NO_2 \cdot C_6H_3Me(OMe) \cdot CH:CH \cdot CO \cdot CH:CH \cdot C_6H_3Me(OMe) \cdot NO_2$ .

This substance was readily prepared under the following conditions: the aldehyde (0.5 gram), dissolved in warm methyl alcohol (5 c.c.), was mixed with acetone (0.5 gram), and, after the addition of potassium hydroxide (50 per cent.: two drops), the yellow mixture was heated to boiling for a few minutes. The liquid rapidly clouded and a voluminous mass of yellow needles separated. These were collected, well washed with methyl alcohol, and the residue recrystallised from acetic acid, in which it was only very sparingly soluble, when it was obtained in fine, yellow needles decomposing at 252°:

0.094 gave 6 c.c.  $N_2$  at 32° and 758 mm.  $N=6.8$ .

$C_{21}H_{20}O_7N_2$  requires  $N=6.8$  per cent.

\* The acid (0.05 gram) which separated from the sodium carbonate solution on acidification was found to be 5-nitro-2-methoxy-m-toluic acid.

*Oxidation of 5-Nitro-2-methoxy-m-tolualdehyde. 5-Nitro-2-methoxy-m-toluic Acid (VI).*

The nitro-aldehyde (1.2 grams) was dissolved in acetone (30 c.c.) and finely powdered potassium permanganate (0.65 gram) was gradually added. The oxidation proceeded readily, and, after the reaction was complete, water was added, the solution boiled, and the manganese dioxide filtered off. The filtrate was concentrated on the water-bath until free from acetone, a trace of unchanged aldehyde removed, and the aqueous solution acidified, when the nitro-acid separated in fine needles. These were collected and crystallised from hot water:

0.2036 gave 12 c.c.  $N_2$  at  $30^\circ$  and 759 mm.  $N = 6.3$ .

$C_9H_9O_5N$  requires  $N = 6.6$  per cent.

5-Nitro-2-methoxy-m-toluic acid crystallises from hot water in glistening, silky needles melting at  $154^\circ$ . It is readily soluble in the ordinary organic solvents with the exception of light petroleum.

The silver salt separated in pale yellow needles, which were somewhat soluble in hot water:

0.2974 gave 0.1007 Ag.  $Ag = 33.8$ .

$C_9H_9O_5Ag$  requires  $Ag = 34.0$  per cent.

For the purposes of comparison, a specimen of 5-nitro-2-methoxy-m-toluic acid was prepared by the methylation of the corresponding hydroxy-acid obtained by the nitration of 2-hydroxy-m-toluic acid (Einhorn and Pfyl, *loc. cit.*). The acid isolated from the methylation melted at  $154^\circ$ , and was identical in every way with the acid prepared by the method described above.

*2-Methoxy-m-toluic Acid (VIII).*

This acid was readily obtained by the oxidation of the corresponding aldehyde by means of potassium permanganate in acetone solution. It separated from hot water in hair-like needles which melted at  $83^\circ$ . It was readily soluble in hot water and in the ordinary organic solvents, somewhat readily so in cold water:

0.0952 gave 0.2266  $CO_2$  and 0.053  $H_2O$ .  $C = 64.9$ ;  $H = 6.2$ .

$C_9H_{10}O_3$  requires  $C = 65.1$ ;  $H = 6.1$  per cent.

The silver salt was obtained as a caseous, white precipitate which was dried at  $100^\circ$  for analysis:

0.37 gave 0.1475 Ag.  $Ag = 39.9$ .

$C_9H_9O_3Ag$  requires  $Ag = 39.6$  per cent.

*Nitration of 2-Methoxy-m-toluic Acid.*

The acid (0.3 gram) was gradually added to nitric acid (D 1.52: 1 gram), the temperature being kept at about 30°. After remaining for ten minutes, the clear solution was poured into water, when the nitro-acid separated and was collected (yield, 0.3 gram). After crystallisation from hot water, it melted at 154°, and this melting point was unaltered on admixture with a specimen of the 5-nitro-acid prepared by the oxidation of the nitro-aldehyde as described above. The 5-nitro-acid appeared to be the sole product of the reaction, since the mother liquors yielded no trace of an isomeride.

*Nitration of 6-Methoxy-m-tolualdehyde (IX). 5-Nitro-6-methoxy-m-tolualdehyde (XI).*

The aldehyde (3 grams) was added slowly to nitric acid (D 1.52: 9 grams), which was kept well cooled in a mixture of salt and ice. The aldehyde dissolved with considerable evolution of gas, and, after remaining for ten minutes, the mixture was poured on ice, when the nitro-aldehyde separated and was collected (yield, 4.2 grams).

5-Nitro-6-methoxy-m-tolualdehyde crystallises from dilute alcohol in small needles melting at 77°. It is readily soluble in all the ordinary organic solvents:

0.1093 gave 7.2 c.c.  $N_2$  at 31° and 760 mm.  $N = 7.1$ .

$C_9H_9O_4N$  requires  $N = 7.2$  per cent.

The semicarbazone crystallised from alcohol in needles which decomposed at 235°:

0.0849 gave 17.4 c.c.  $N_2$  at 31° and 760 mm.  $N = 22.0$ .

$C_{10}H_{13}O_4N_4$  requires  $N = 22.2$  per cent.

*5:5'-Dinitro-4:4'-dimethoxydi-3-methylstyryl Ketone.*

This substance was prepared in a similar manner to the isomeride described on p. 778. It crystallises from acetic acid in yellow needles melting at 214°:

0.0526 gave 3.4 c.c.  $N_2$  at 30° and 759 mm.  $N = 6.9$ .

$C_{21}H_{20}O_4N_2$  requires  $N = 6.8$  per cent.

*5-Nitro-6-methoxy-m-toluic Acid (XII).*

This acid was readily obtained when the nitro-aldehyde was oxidised with potassium permanganate in acetone solution. For analysis, it was crystallised from dilute alcohol:

0.1752 gave 11.2 c.c.  $N_2$  at  $31^\circ$  and 760 mm.  $N=6.8$ .

$C_9H_9O_3N$  requires  $N=6.6$  per cent.

5-Nitro-6-methoxy-m-toluic acid crystallises in colourless, felted needles melting at  $180-181^\circ$ , and softening slightly at  $175^\circ$ . It is very sparingly soluble in cold water, somewhat more readily so in hot; it is very readily soluble in chloroform, acetic acid, or ethyl acetate, more sparingly so in benzene.

The barium salt crystallised in sparingly soluble, curious nodular masses of needles; the calcium salt was obtained in stellate clusters of needles which were readily soluble in hot water; the silver salt separated as a granular, white precipitate:

0.2272 gave 0.0772 Ag.  $Ag=34.0$ .

$C_9H_8O_3Na$  requires  $Ag=34.0$  per cent.

The methyl ester,  $C_{10}H_{11}O_3N$ , crystallised from dilute methyl alcohol in silky needles melting at  $47^\circ$ .

#### Nitration of 6-Methoxy-m-toluic Acid (X).

The finely powdered acid (1.4 grams) was gradually added to nitric acid (D 1.52:5 grams), the temperature being kept between  $30^\circ$  and  $35^\circ$ . The acid dissolved with considerable evolution of gas, and, after remaining for ten minutes, the mixture was poured into water and the solid which separated was collected and triturated with dilute sodium carbonate solution, a considerable quantity of a neutral substance, A (0.62 gram), remaining undissolved. This was separated, the filtrate acidified, and the acid which was deposited (0.97 gram) crystallised from dilute alcohol, when it was obtained in fine needles melting at  $180-181^\circ$ , this melting point being unaltered on admixture with a specimen of the acid obtained by the oxidation of the nitro-aldehyde. The neutral substance A was purified by crystallisation from methyl alcohol, from which it separated in glistening needles melting at  $69^\circ$ . For analysis, it was dried in a vacuum:

0.1404 gave 11 c.c.  $N_2$  at  $30^\circ$  and 759 mm.  $N=8.5$ .

$C_9H_9O_3N$  requires  $N=8.4$  per cent.

This substance would appear to be 6-nitro-o-tolyl methyl ether (XIII). It was attacked by a hot alkaline solution of potassium permanganate only with great difficulty, but it was found to be readily oxidised by chromic acid under the following conditions: the nitro-compound (0.25 gram) was dissolved in concentrated sulphuric acid (1 c.c.) and gradually treated with chromic acid (0.3 gram) dissolved in concentrated sulphuric acid (2 c.c.), the temperature being kept at about  $40^\circ$ . When the reaction was

complete, water was added, the nitro-acid which separated was collected, dissolved in a little dilute sodium carbonate solution, and filtered from a little unattacked material. On acidifying the alkaline filtrate, the nitro-acid separated in fine, prismatic needles which melted at 159—160°. After crystallisation from hot water, in which it was readily soluble, it melted at 161°. This acid was probably 6-nitro-2-methoxybenzoic acid (XIV), an acid which does not appear to have been described previously. It was not identical with 5-nitro-2-methoxybenzoic acid, which also melts at this temperature (Simonsen and Rau, T., 1917, 111, 228), since a mixture of the two acids melted at about 140°. Unfortunately, this new acid was not obtained in sufficient quantity for a detailed examination.

In conclusion, the author wishes to thank Mr. M. Gopala Rau, M.A., for his assistance in the analytical work.

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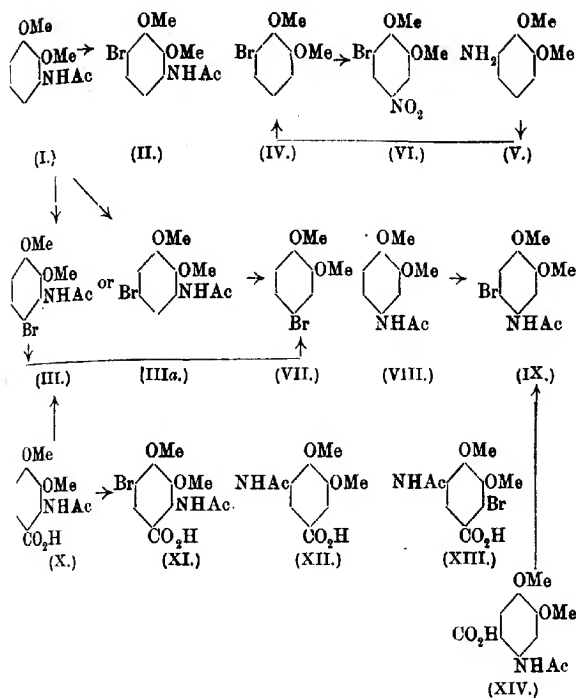
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### LXVIII.—*The Bromination of some Derivatives of Veratrole.*

By JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU.

IN previous communications (T., 1917, 111, 69, 220; this vol., p. 22), the results of experiments were described on the nitration of some acetylamino-derivatives of veratrole and methoxybenzoic acids, and attention was directed to the relative orientating influence of methoxy-groups having positive or negative groups in the ortho- or para-positions. In continuation of these experiments, it appeared to us to be a matter of some interest to investigate the effect of bromination on the same series of compounds in order to determine whether substitution would proceed similarly. When these experiments were nearing completion, a paper by Jones and Robinson (T., 1917, 111, 903) appeared which has anticipated our work in some directions.

We selected for our experiments the two isomeric acetylamino-veratroles and the three acetylaminoveratric acids, and the results obtained are shown diagrammatically below.



The bromination was performed either in chloroform or in glacial acetic acid solution, the sparingly soluble bromo-amide which separated was decomposed with water, and the product isolated in a suitable manner. As will be observed, the bromine always entered the nucleus in the para-position with respect to the acetyl-amino-group, except in the case of 6-acetylaminoveratric acid (XIV), when, this position being already occupied, the carboxyl group was eliminated with the formation of 5-bromo-4-acetylaminoveratrole (IX). Only in one case was the formation of an isomeride detected, namely, when 3-acetylaminoveratrole (I) was brominated under special conditions (see p. 786). It has not, unfortunately, proved possible to orientate this isomeride, which must be either the 4- or 5-bromo-derivative (III or IIIa), since on the elimination of the amino-group it yielded 4-bromoveratrole. From analogy, it is most probably the 4-isomeride, and this view receives

support from the fact that traces of this bromide were also formed during the bromination of 2-acetylaminoveratric acid (X).

The constitution of the main product of the bromination of 3-acetylaminoveratrole, 6-bromo-3-acetylaminoveratrole (II), was determined by eliminating the amino-group with the formation of 3-bromoveratrole (IV), a substance which was also prepared from 3-aminoveratrole (V), the bromide from each source being converted by nitration into 6-bromo-4-nitroveratrole (VI), which has already been described by Jones and Robinson (*loc. cit.*, p. 918).

The bromination of 4-acetylaminoveratrole (VIII) has already been investigated by Jones and Robinson (*loc. cit.*, p. 913), who found that 5-bromo-4-acetylaminoveratrole (IX) was formed. This result we are able to confirm, but we have found that the compound melted at 127–128°, and not at 140° as stated by these authors. In view of the ease with which this substance was obtained in a pure state, it appears to us probable that the melting point quoted by Jones and Robinson is due to a misprint.\*

The determination of the constitution of the isomeric bromo-acetylaminoveratric acids (XI, XII) obtained by the bromination of 2- and 5-acetylaminoveratric acids (X, XII) offered no difficulty, the corresponding bromoveratric acids being obtained on displacement of the amino-group by hydrogen.

In view of the fact that the formation of the bromo-amide always preceded substitution in the nucleus, which was therefore indirect, these experiments cannot be said to have thrown any light on the mechanism of the nitration of this type of substance. If indirect substitution directed by the methoxy-group does take place on nitration, it should prove possible by choice of suitable conditions to isolate this salt, and it is hoped to make further experiments with the object of throwing light on this problem.

#### EXPERIMENTAL.

##### *Bromination of 3-Acetylaminoveratrole (I). 6-Bromo-3-acetylaminoveratrole (II).*

In one experiment, 3-acetylaminoveratrole (3 grams) was dissolved in chloroform (9 c.c.), and to the ice-cold solution bromine (2.64 grams) dissolved in chloroform (3 c.c.) was gradually added, when bromination took place readily with the separation of the sparingly soluble yellow bromo-amide. After remaining for fifteen minutes, the precipitate was decomposed by the addition of water, the chloroform solution separated, washed with a little

\* Prof. Robinson has since informed me that this is the case.—J. L. S.

dilute alkali, dried, and evaporated, when a theoretical yield of the bromoacetylamine was obtained. It was purified by crystallisation from dilute acetic acid:

0.1942 gave 0.1332 AgBr. Br=29.3.

0.1544 „ 7.6 c.c. N<sub>2</sub> at 30° and 758 mm. N=5.3.

C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>NBr requires Br=29.2; N=5.1 per cent.

6-Bromo-3-acetylaminoveratrole crystallises in prismatic needles melting at 78°. It is readily soluble in all the ordinary organic solvents with the exception of benzene and light petroleum. The same bromoacetylamine was found to be the sole product when glacial acetic acid was used as the solvent in place of chloroform.

6-Bromo-3-aminoveratrole was formed when the acetyl derivative was heated on the water-bath for some hours with hydrochloric acid (50 per cent.). It crystallises from dilute methyl alcohol in colourless needles melting at 66°, and is readily soluble in the ordinary organic solvents:

0.119 gave 6.6 c.c. N<sub>2</sub> at 30° and 759 mm. N=6.0.

C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>NBr requires N=6.0 per cent.

The benzoyl derivative crystallised from dilute alcohol in minute, radiating needles melting at 75°:

0.1935 gave 8.0 c.c. N<sub>2</sub> at 30° and 760 mm. N=4.4.

C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>NBr requires N=4.1 per cent.

### 3-Bromoveratrole (IV) and 6-Bromo-4-nitroveratrole (VI).

1. For the determination of the constitution of the bromo-amide described above, it was necessary to prepare 3-bromoveratrole. This substance, which does not appear to have been previously described, was readily obtained when 3-aminoveratrole (Gibson, Simonsen, and Rau, *loc. cit.*, p. 79) was diazotised and treated with cuprous bromide in the usual manner. It was purified by distillation in a current of steam and subsequent distillation under diminished pressure, when it was obtained as a somewhat viscid oil boiling at 114°/5 mm.:

0.1287 gave 0.1117 AgBr. Br=36.9.

C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>Br requires Br=36.9 per cent.

\* When 3-bromoveratrole was dissolved in acetic acid and treated with nitric acid (D 1.4), it yielded 6-bromo-4-nitroveratrole, which crystallised from alcohol in needles melting at 112–113°, and was found by direct comparison to be identical with the substance described by Jones and Robinson (*loc. cit.*, p. 918) (Found: N=5.5. Calc.: N=5.3 per cent.).

11. 3-Bromoveratrole was also formed when 6-bromo-3-amino-



veratrole (see above) was diazotised in alcoholic solution with *amyl* nitrite in the usual manner. It was identified by conversion into 6-bromo-4-nitroveratrole melting at 112°–113° (Found: N=5.5. Calc.: N=5.3 per cent.).

4- or 5-Bromo-3-acetylaminoveratrole (III or IIIa).

For the preparation of this substance, the following method was found to be the most convenient. The acetylamine (5 grams) was dissolved in acetic acid (50 per cent.:20 c.c.) and bromine (4.2 grams) was gradually added to the well-cooled solution. When bromination was complete, the mixture was diluted with water and ammonia added until a nearly neutral solution was obtained. On remaining overnight, the bromination product, A, separated; this was collected and the filtrate repeatedly extracted with ether. The ether was evaporated and the residual oil triturated with cold acetone, when a sparingly soluble solid remained. This was mixed with the product A (see above) and purified by crystallisation from acetone, when it separated in well-defined octahedra melting at 151° (yield, 2 grams):

0.1966 gave 0.136 AgBr. Br=29.4.

0.1842 „ 9.4 c.c. N<sub>2</sub> at 30° and 756 mm. N=5.3.

C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>NBr requires Br=29.2; N=5.1 per cent.

4- or 5-Bromo-3-acetylaminoveratrole is readily soluble in alcohol or acetic acid, more sparingly so in benzene, acetone, ether, or light petroleum.

The corresponding *amine* was obtained by heating the acetyl derivative for one hour on the water-bath with sulphuric acid (50 per cent.). It separated from dilute methyl alcohol in colourless needles melting at 49°:

0.1268 gave 0.1023 AgBr. Br=34.4.

C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>NBr requires Br=34.4 per cent.

The *benzoyl* derivative, C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>NBr, crystallised from dilute alcohol in needles melting at 146°.

The *platinochloride* separated from dilute hydrochloric acid in aggregates of yellowish-brown prisms which darkened at 200° and gradually decomposed when heated above this temperature:

0.1659 gave 0.0402 Pt. Pt=24.2.

(C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>NBr)<sub>2</sub>H<sub>2</sub>PtCl<sub>4</sub> requires Pt=24.3 per cent.

When the above-mentioned bromo-amine was diazotised, it yielded 4-bromoveratrole, which was identified by conversion into 4-bromo-5-nitroveratrole melting at 123° (Jones and Robinson).

*loc. cit.*, give  $125^{\circ}$  as the melting point of this substance (Found:  $N=5.3$ . Calc.:  $N=5.2$  per cent.).

The acetone solution from which the 4- or 5-bromo-3-acetylaminoveratrole had been separated was evaporated, and the residue (5.5 grams) was repeatedly crystallised from alcohol, when a substance melting at  $78^{\circ}$  was isolated and found by direct comparison to be 6-bromo-3-acetylaminoveratrole.

*Bromination of 4-Acetylaminoveratrole (VIII). 5-Bromo-4-acetylaminoveratrole (IX).*

As has already been mentioned in the introduction (p. 784), the bromination of 4-acetylaminoveratrole has already been investigated by Jones and Robinson (*loc. cit.*, p. 913), who found that 5-bromo-4-acetylaminoveratrole was formed. We have investigated this bromination both in chloroform and in acetic acid solutions, when the 5-bromo-derivative was obtained as the sole product. It crystallised from hot water in long, slender needles which melted at  $127-128^{\circ}$ . Attention has already been directed to the discrepancy between this melting point and that found by Jones and Robinson:

0.1981 gave 0.1352 AgBr.  $Br=29.3$ .

$C_{10}H_{12}O_3NBr$  requires  $Br=29.2$  per cent.

5-Bromo-4-aminoveratrole, which has not been described previously, was obtained only with considerable difficulty, owing to the ease with which it decomposed. Ultimately, the following method was found to be fairly satisfactory. The bromoacetylamine was dissolved in a methyl-alcoholic solution of potassium hydroxide (15 per cent. KOH) and heated on the water-bath for three hours, the excess of potassium hydroxide removed by carbon dioxide, the solution filtered, and the methyl alcohol evaporated in a vacuum at the ordinary temperature. The residue was extracted with ether, the ether evaporated, when the base was obtained as a viscid oil which rapidly crystallised. After draining a porous porcelain, it was recrystallised from dilute methyl alcohol, from which it separated in colourless needles melting at  $51^{\circ}$ . When exposed to the air, the base rapidly darkened in colour:

0.0844 gave 0.0682 AgBr.  $Br=34.4$ .

$C_8H_{10}O_2NBr$  requires  $Br=34.4$  per cent.

The benzoyl derivative,  $C_{15}H_{14}O_3NBr$ , crystallised in needles melting at  $142^{\circ}$ .

The constitution of this bromo-amine was readily determined by conversion into 4:5-dibromoveratrole. The bromo-amine (1 gram) is dissolved in hydrobromic acid (30 per cent.: 5 c.c.) and diazo-

tised by the addition of sodium nitrite (0.4 gram). After remaining in the cold for half an hour, the mixture was poured into hydrobromic acid (5 c.c.) containing a little copper powder and allowed to remain in the cold overnight. The solution was warmed on the water-bath, extracted with ether, the ether evaporated, and the residue crystallised from alcohol, when 4:5-dibromoveratrole separated in needles melting at 92°, which melting point was not changed on admixture with a specimen of the compound obtained from a different source.

*Bromination of 2-Acetylaminoveratric Acid (X). 5-Bromo-2-acetylaminoveratric Acid (XI).*

I. 2-Acetylaminoveratric acid (2 grams) was suspended in acetic acid (4 c.c.) and mixed with bromine (1.3 grams) dissolved in acetic acid (2 c.c.); the mixture was sealed up and allowed to remain, with occasional shaking, for twenty-four hours, when the colour of the bromine had completely disappeared and a yellow, unstable bromo-amide had separated. On the addition of water, a clear solution was obtained, from which the bromo-acid gradually crystallised. This was collected, and a further quantity obtained by extracting the filtrate with ether (yield, 2.1 grams). On trituration with dilute sodium carbonate solution, a small quantity of a neutral substance (0.1 gram) remained undissolved. This crystallised from alcohol in needles melting at about 168°, but it was not obtained in sufficient quantity for investigation. The acid which separated from the alkaline filtrate on acidification was found to be quite homogeneous, and was purified by crystallisation from ethyl acetate:

0.1534 gave 0.0908 AgBr. Br=25.2.

$C_{11}H_{12}O_5NBr$  requires Br=25.1 per cent.

5-Bromo-2-acetylaminoveratric acid separates in fine needles melting at 188—189°. It is readily soluble in acetone, alcohol, ethyl acetate, or chloroform, more sparingly so in water, benzene, or ether, and very sparingly so in light petroleum.

II. 2-Acetylaminoveratric acid (2 grams) was mixed with chloroform (4 c.c.) and treated with bromine (1.3 grams) dissolved in chloroform (2 c.c.); the bromo-amide gradually separated, and, after remaining for twenty-four hours, the mixture was treated with water, the chloroform separated, washed with a little dilute alkali, dried, and evaporated, when a small quantity of a neutral substance remained. This was crystallised from a little dilute methyl alcohol, when it crystallised in octahedra melting at 151°, and was found to be 4- or 5-bromo-3-acetylaminoveratrole.

The alkaline washings yielded on acidification 5-bromo-2-acetylaminoveratric acid.

5-Bromo-2-aminoveratric acid was obtained when the acetyl derivative was hydrolysed with either hydrochloric acid or concentrated sulphuric acid. It crystallises from alcohol in colourless prisms melting at 158—159°:

0.1114 gave 5.6 c.c.  $N_2$  at 31° and 758 mm.  $N = 5.4$ .

$C_9H_{10}O_4NBr$  requires  $N = 5.1$  per cent.

The constitution of this amino-acid was readily proved by the elimination of the amino-group, when 5-bromoveratric acid melting at 191° was obtained (Found:  $Br = 30.5$ . Calc.:  $Br = 30.6$  per cent.).

*Bromination of 5-Acetylaminoveratric Acid (XII).*

*2-Bromo-5-acetylaminoveratric Acid (XIII).*

The acid (2 grams) was dissolved in acetic acid (4 c.c.) and treated with the calculated quantity of bromine dissolved in a little acetic acid. The clear solution rapidly became cloudy, and a voluminous precipitate of the reddish-yellow bromo-amide separated. After remaining for ten minutes, water was carefully added, when a clear solution was obtained, from which the bromo-acid slowly crystallised. This was collected and recrystallised from dilute alcohol, from which it separated in fine needles:

0.1862 gave 0.1096 AgBr.  $Br = 25.1$ .

$C_{11}H_{12}O_5NBr$  requires  $Br = 25.1$  per cent.

2-Bromo-5-acetylaminoveratric acid melts at 221°. It is readily soluble in hot alcohol or acetone, more sparingly so in the cold solvents; in water or benzene it is sparingly soluble.

On hydrolysis of the acetyl-amino-acid with hydrochloric acid (50 per cent.), the amino-acid was obtained as a viscid oil which rapidly crystallised. It was recrystallised from dilute alcohol, from which it separated in glistening prisms melting at 183°. It is readily soluble in hot alcohol or acetone, but only sparingly so in water, chloroform, or benzene:

0.151 gave 0.1021 AgBr.  $Br = 28.8$ .

$C_9H_{10}O_4NBr$  requires  $Br = 28.9$  per cent.

When diazotised in alcoholic solution with amyl nitrite, it yielded 2-bromoveratric acid, which after crystallisation from methyl alcohol melted at 201—202° (Found:  $Br = 30.2$ . Calc.:  $Br = 30.6$  per cent.).

*Bromination of 6-Acetylaminoveratric Acid (XIV).**5-Bromo-4-acetylaminoveratrole (IX).*

The finely divided acid (2 grams) was suspended in chloroform and the calculated quantity of bromine dissolved in chloroform gradually added. The bromine was rapidly absorbed, and simultaneously a small amount of gas (carbon dioxide) was evolved. After remaining overnight, water was added to the pasty mass, when a vigorous evolution of gas was observed. A small quantity of unchanged acid was removed by filtration, the chloroform separated, washed with a little dilute alkali, dried, and evaporated. The deep brown residue rapidly solidified to a hard, crystalline cake, and was purified by crystallisation from hot water, from which it separated in slender, colourless needles melting at 127—128°, and was identical in every way with the compound obtained by the bromination of 4-acetylaminoveratrole. No trace of any other product could be isolated:

0.1144 gave 0.0775 AgBr. Br = 28.9.

$C_{10}H_{12}O_3NBr$  requires Br = 29.2 per cent.

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# LXIX.—*The Electrical Conductivity of Acids and Bases in Aqueous Solutions.*

By JNANENDRA CHANDRA GHOSH.

IN previous papers (this vol., pp. 449, 627, 707), it has been shown that the variation of equivalent conductivity with dilution, in the case of all binary univalent salts, is represented by the equation

$$\frac{N \cdot E^2 \sqrt{2N}}{D \cdot \sqrt{V}} = 2RT \log_e \frac{\mu_{\infty}}{\mu_v} \quad \dots \quad (1)$$

where  $N$  is Avogadro's number,  $E$  the absolute charge on an ion,  $D$  the dielectric constant of the solvent, and  $V$  the dilution.

*Abnormally High Values of Activity-coefficients of Acids and Bases.*—Aqueous solutions of strong acids like hydrochloric or nitric acids, and of strong bases like sodium or potassium hydroxides, however, prove exceptions to the above rule. This irregular behaviour will be at once evident from table I, where the values of the activity-coefficients calculated from equation (1) are com-

pared with the observed values (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 474).

TABLE I.

	$V =$	10.	20.	50.	100.	200.	500.
$\mu_e$ calc. ....		0.844	0.875	0.906	0.924	0.940	0.955
$\mu_x$							
$\frac{\mu_e}{\mu_x}$ obs. for HCl.....		0.925	0.944	0.962	0.972	0.981	0.988
$\frac{\mu_e}{\mu_x}$ obs. for KOH ...		0.887	0.910	0.933	0.945	—	0.970

This irregularity disappears as we pass from the aqueous to non-aqueous solutions of strong acids. In alcoholic solutions, for example, equation (1) is exactly followed. In table II, the observed values of the molecular conductivity of hydrochloric acid in methyl alcohol are taken from the work of Goldschmidt and Thuesen (*Zeitsch. physikal. Chem.*, 1912, **81**, 32). For dilute solutions, the agreement between observed and calculated values is always within 1 per cent., and the validity of equation (1) is therefore proved beyond doubt.

TABLE II.  $T = 25^\circ$ .

	$V =$	40.	80.	160.	320.	640.	
$\mu_x$ calc. from $\mu_{30} = 192.2$	$\mu_e$	calc.	142.5	151.8	159.5	166.7	
$\mu_x$ obtained by extrapolation = 192.1							
	$\mu_e$	obs.	141.0	151.8	160.5	167.2	171.9

*Abnormally High Values of the Electrical Conductivity of Acids and Bases.*—It has always appeared remarkable that the values of the equivalent conductivity of acids and bases in aqueous solutions are not of the same order of magnitude as those of other salts. Thus the conductivities of hydrogen and hydroxyl ions in aqueous solutions are 318 and 175 respectively at  $18^\circ$ , whilst those of the other ions never exceed 70. In non-aqueous solutions, again, this abnormality is not observed. Thus in ethyl alcohol, the conductivities of hydrogen and hydroxyl ions are 32.1 and 16.5, whilst those of potassium and ammonium ions are 21.5 and 20 respectively (Godlewski, *Zeitsch. physikal. Chem.*, 1905, **51**, 751; Hägglund, *Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 11). Here the values are of the same order. This is also true for solutions in other solvents, for example, methyl alcohol or acetone.

*The Conductivity of Aqueous Solutions of Acids and Bases—not entirely a Convection Process.*—It is thus evident that the abnormal conductivities of hydrogen and hydroxyl ions, in aqueous solutions,

are somehow related to the high values of the activity-coefficients of acids and bases, both these abnormalities disappearing when the solvent medium is other than water. Equation (1) has a good theoretical basis, and it appears more reasonable to assume that the observed ratio  $\frac{\mu_n}{\mu_\infty}$  for acids and bases in aqueous solutions is

not a real expression for the activity-coefficient, than to impugn its validity. It appears to the author that the observed conductivity of hydrogen and hydroxyl ions in water is the additive effect of two separate and independent processes, namely, (1) the transference of electricity by the convection of charged bodies, and (2) the transference of electric charge through molecules of water by the alternate processes of dissociation and recombination during impact with hydrogen or hydroxyl ion.

The first process is, of course, the ordinary method of electrolytic conduction met with in salt solutions. Here, only the free ions take part in the transference of electricity, and their number is given by the equation

$$N' = 2N \cdot e^{-\frac{A}{2\pi r}} \dots \dots \dots (2)$$

The mechanism of transport of electricity through molecules of water may be conceived as follows.

A molecule of water is capable of dissociating into hydrogen and hydroxyl ions, the only ions that possess abnormal conductivity. Now, in a dilute solution of hydrochloric acid the hydrogen ion is surrounded by water molecules on all sides. It appears probable that when a hydrogen ion strikes against a molecule of water, the latter in some cases undergoes dissociation. The hydrogen ion thus produced carries away the electric charge by convection, whilst the hydroxyl ion of the water molecule combines with the impinging hydrogen ion to generate a molecule of water. The conception of the process is similar to that imagined by Grotthuss to explain the phenomenon of electrolytic conduction. It may well be that the hydrogen atom of the water molecule, which is farthest from the point of impact, shoots off as a charged particle, and if the process of dissociation and recombination is instantaneous, the electric charge (+*E*) appears to be carried instantaneously through a distance proportional to the diameter *S* of the water molecule. Thus at each impact attended with dissociation a distance  $K_1 S$  is saved, where  $K_1$  is always a fractional quantity. The result is that the hydrogen ion appears to move with a velocity much greater than its true characteristic velocity. Now let  $U_H$  be the real velocity of the hydrogen ion. The total number of impacts with water molecules per second is  $K_2 N \cdot \pi \cdot S_1^2 U_H \cdot n$ , where *n* is the

number of water molecules in a c.c. and  $S_1$  the diameter of the hydrogen ion. The number of impacts attended with dissociation is  $K_3 \cdot K_2 \cdot N \cdot \pi \cdot S_1^2 U_{H^+} \cdot n$ , and the distance saved per second =  $K_1 \cdot S \cdot K_3 \cdot K_2 \cdot N \cdot \pi \cdot S_1^2 \cdot U_{H^+} \cdot n = C$  at a constant temperature, since  $K_1$ ,  $K_2$ ,  $K_3$ ,  $U_{H^+}$ , have always the same value at constant temperature.  $C$  also does not vary with dilution if  $n$  and  $N$  do not vary. Now in the case of dilute solutions, the number of solvent molecules in a c.c. may always be regarded as constant, independent of concentration, without introducing much error. Since, according to the theory developed before, strong electrolytes are completely dissociated in dilute solutions, the number of hydrogen ions in a solution containing a gram-molecule is always constant. Whilst in the first process—the transference of electric charge by convection—only the free hydrogen ions take part, this is not the case in the second process. Here it stands more to reason to assume that all the hydrogen ions are equally efficient, for, considering that some of the hydrogen ions are stationary, there is nothing to prevent their collision with water molecules, for the latter are always free to move. In fact, the inactive hydrogen ions are always capable of vibratory motion. The distance  $C$  saved per second is thus independent of dilution.

Hence, for solutions of hydrochloric acid, on the basis that the activity-coefficient  $\alpha$  at any dilution is the same as that of univalent binary salts, we get

$$\mu_c = \alpha(U_{H^+} + U_{Cl}) + C_1 \quad \dots \quad (3)$$

where  $\alpha$  is the activity-coefficient at dilution  $v$ , and  $C_1$  a constant independent of dilution.  $\alpha$  can always be calculated from equation (1).

Again,

$$\mu_\alpha = U_{H^+} + U_{Cl} + C_1 \quad \dots \quad (4)$$

From equations (3) and (4),

$$U_{H^+} = \mu_\alpha - \frac{\mu_c - (1 - \alpha)U_{Cl}}{1 - \alpha} \quad \dots \quad (5)$$

and

$$C_1 = \mu_\alpha - U_{H^+} - U_{Cl} \quad \dots \quad (6)$$

$U_{H^+}$ , the real ionic mobility of the hydrogen ion, and  $C_1$ , the conductivity due to the second process, can thus at once be calculated from available data.

*Experimental Confirmation of the above Hypothesis.*—The experimental data on the conductivity of acids must always yield the same value of  $C_1$  and  $U_{H^+}$  provided the acid is a strong electrolyte. This expectation has been fully realised. Thus, for a solution of



hydrochloric acid at dilution 10 and temperature  $25^{\circ}$ ,  $\mu_{\alpha}=390.4$ ,  $\mu_{\alpha}=426$ ,  $U_{cr}=75.8$ , and  $\alpha=0.844$ , whence  $U_{H^+}=152.4$  and  $C_1=197.8$ .

Again, for solutions of nitric acid, at dilution 10, the available data give for  $U_{H^+}$  151.3 and 198.8 for  $C_1$  (Noyes and Falk, *loc. cit.*). The values of  $U_{H^+}$  and  $C_1$  obtained from the data on the conductivity of hydrochloric and nitric acids therefore agree within 1 per cent. We may take 152 as the mean value of  $U_{H^+}$  and 198.5 as that of  $C_1$ . The real mobility of hydrogen ion is therefore of the same order of magnitude as those of the other ions. The second process is thus responsible for the transference of about half the electric current in acid solutions.

The values of  $U_{H^+}$  and  $C_1$  having once been determined, it is possible to calculate the molecular conductivity of any strong acid at any dilution from equation (3). Tables III and IV show how the calculated values agree with the observed ones.

In table III, the observed values are taken from the work of Noyes and Falk (*loc. cit.*), whilst the data in table IV are obtained from a paper by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 436).

TABLE III.

	$V=$	20.	100.	500.	1000.	2000.
HCl .....	$\mu_{\alpha}$ calc.	397.6	408.9	416.5	418.4	—
	$\mu_{\alpha}$ obs.	398.4	410.5	418.5	420.4	—
HNO <sub>3</sub> .....	$\mu_{\alpha}$ calc.	393.1	404.5	411.0	—	415.0
	$\mu_{\alpha}$ obs.	393.3	406.0	413.0	—	417.0

TABLE IV.

	$V=$	100.	400.	111.	1600.
Naphthalene- $\beta$ -sulphonic acid .....	$\mu_{\alpha}$ calc.	637.2	372.4	375.3	376.3
	$\mu_{\alpha}$ obs.	367.4	374.9	376.9	377.4
Toluene- $p$ -sulphonic acid .....	$\mu_{\alpha}$ calc.	369.9	375.0	377.6	378.5
	$\mu_{\alpha}$ obs.	368.4	375.3	378.2	379.0

The agreement between the observed and calculated values is always within 0.5 per cent.

The real values of  $U_{OH^-}$  and  $C_1$  for bases can also be obtained in the same way. Thus, at dilution 10,  $\mu_{\alpha}$  for potassium hydroxide is 213;  $\mu_{\alpha}$  is 240.2. From these data, the value of  $U_{OH^-}$  is 109 and of  $C_1$  for bases 66. Table V shows how exactly the observed values of the molecular conductivity of potassium hydroxide agree with those calculated from equation (3).

TABLE V.

	$V =$	20.	50	100.	500.
OH.....	$\left\{ \begin{array}{l} \mu_{\pm} \text{ calc.} \\ \mu_{\pm} \text{ obs.} \end{array} \right.$	218.4	224.0	227.1	232.5
		219.0	225.0	228.0	233.0

Arrhenius has already suggested "that the exceptionally great conductivity of these ions ( $\text{H}^+$  and  $\text{OH}^-$ ) in water is probably due only to the fact that they are the two ions into which water is electrolytically decomposed" ("Theories of Solution," p. 138). In the foregoing pages, an attempt has been made to develop a quantitative explanation of the abnormal mobility of hydrogen and hydroxyl ions by assuming that an electric charge can be transferred almost instantaneously through water molecules during impact with these ions by the converse processes of dissociation and recombination taking place alternately.

*A General Hypothesis for all Electrolytes.*—The electrolytes can be classified into three groups, namely, (1) consisting of strong electrolytes, (2) containing acids of intermediate strength, "transition electrolytes," and (3) consisting of weak acids and bases where Ostwald's dilution law holds good.

For the first group we have the following empirical laws:

$$\mu_{\pm} = \mu_{\infty} - a \sqrt{C} \quad (\text{Kohlrausch, } \textit{Ann. Phys. Chem.}, 1885, [\text{iii}], 26, 161) \quad (7)$$

and

$$i = 2 - b - \sqrt[3]{C} \quad (\text{Noyes and Falk, } \textit{J. Amer. Chem. Soc.}, 1910, 32, 101) \quad (8)$$

Equation (1) becomes identical with Kohlrausch's empirical law in the case of dilute solutions where  $\mu_{\pm}$  is only slightly less than  $\mu_{\infty}$ . Thus, equation (1) may be put in the form

$$\frac{K}{\sqrt[3]{V}} = \log \frac{\mu_{\infty}}{\mu_{\pm}}$$

or

$$K \sqrt[3]{C} = \frac{\mu_{\infty} - \mu_{\pm}}{\mu_{\infty}} = 1 - \frac{\mu_{\pm}}{\mu_{\infty}} \quad (9)$$

or

$$\mu_{\pm} = \mu_{\infty} (1 - K \sqrt[3]{C}) = \mu_{\infty} - a \sqrt[3]{C},$$

Again, the activity-coefficient

$$\alpha = \frac{\mu_{\pm}}{\mu_{\infty}} = 1 - K \sqrt[3]{C} \quad (10)$$

Noyes and Falk's empirical law can easily be derived by apply-

ing Clausius's virial theorem to salt solutions. It has already been shown that

$$\begin{aligned} i &= n \left\{ 1 - \frac{1}{3} \log_e \frac{\mu_\alpha}{\mu_v} \right\} \dots \dots \dots (11) \\ &= n \left\{ 1 - \frac{1}{3} K \sqrt{C} \right\} \\ &= n - \frac{1}{3} n \cdot K \cdot \sqrt{C} \\ &= 2 - b^2/C, \text{ for binary salts where } n=2. \end{aligned}$$

Whilst the strong electrolytes of group 1 belong to the limiting case, we have, for the other two groups, as in Arrhenius's original theory, both undissociated molecules and ions in solution. The law of mass action in its original form is, however, not applicable to electrically charged bodies. It requires modification in the sense that only the free ions take part in the equilibrium. It is only the fraction of the total number of ions which, by virtue of their kinetic energy, can overcome the force of electrostatic attraction, that really matter. They only are free to move, and hence have the chance of colliding with one another. From the kinetic point of view, therefore, only these free ions are to be taken into consideration in applying the law of mass action to the process of electrolytic dissociation. Thus, if  $x$  is the fraction of a gram-molecule of acid, which has undergone dissociation into ions, the law of mass action is not expressed by the equation

$$\frac{x^2}{(1-x)V} = K,$$

but by the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K \dots \dots \dots (12)$$

where  $\alpha$  is the activity-coefficient at the ionic concentration  $\frac{x}{V}$

Now,  $\alpha$  for any dilution can be calculated from equation (1) or (10). In the case of weak acids belonging to the third group,  $\alpha$  is generally very small,  $\frac{x}{V}$  becomes always negligibly small, and hence  $\alpha$  is very nearly equal to one at all dilutions. For very weak acids, therefore, equation (12) becomes identical with Ostwald's dilution law.

*A Dilution Formula for Transition Electrolytes.*—Here the activity-coefficient  $\alpha$  is not always equal to one, and the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K,$$

must be applied as such. According to the ideas developed before,

the equivalent conductivity of an acid of intermediate strength may be equated thus:

$$\mu_v = x \cdot 198.5 + \alpha x (U_{H^+} + U_{Anion}) \quad (13)$$

where  $x$  is the gram-equivalent of total hydrogen ion and  $U_{H^+} = 152$  at  $25^\circ$ , or

$$\mu_v = x \cdot 198.5 + (1 - K^2/C)x \cdot (U_{H^+} + U_{Anion}) \text{ from equation (10)}$$

$$= x(198.5 + U_{H^+} + U_{Anion}) - K \left( \frac{x}{V} \right)^2 \cdot x \cdot (U_{H^+} + U_{Anion})$$

$$\text{or since } c = \frac{x}{V}$$

$$= x \cdot \mu_\infty - \frac{K}{2V} \cdot x^2 \cdot (U_{H^+} + U_{Anion}).$$

The equation contains only one unknown quantity,  $x$ , and hence it admits of a solution. The real value of  $x$  can, however, be easily obtained with great accuracy by the method of successive approximation.  $x$  having thus been determined, it is easy to calculate  $\alpha$  at concentration  $\frac{x}{V}$ . Hence all the factors for verifying the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K,$$

can be had from the conductivity data. In tables VI, VII, VIII, and IX four acids have been chosen in the order of increasing strength to illustrate the validity of the above equation. The values of molecular conductivity have been taken from the very accurate work of Kendall (*loc. cit.*). According to this author,  $M$  for the hydrogen ion at  $25^\circ$  is 347, whilst the value obtained by Noyes and Falk as the mean of the data given by various workers is 350. In the following tables, the latter value has been accepted as true.

TABLE VI.

Cyanoacetic Acid.  $\mu_\infty = 389.1$  at  $25^\circ$ .

$V$ .	$\mu_v$	$x$ .	$\alpha$ .	$K$ .
16.82	88.0	0.2370	0.9158	0.00365
33.64	117.0	0.3120	0.9260	0.00361
67.28	152.5	0.4050	0.9352	0.00358
134.56	193.9	0.5125	0.9442	0.00357
269.10	238.7	0.6283	0.9524	0.00358
538.20	282.6	0.7409	0.9606	0.00363
1076.40	320.0	0.8361	0.9673	0.00368

TABLE VII.

*o*-Nitrobenzoic Acid.  $\mu_{\infty} = 382.2$  at  $25^{\circ}$ .

V.	$\mu_{\infty}$	$\alpha$ .	$\alpha$ .	K.
32.0	139.7	0.3810	0.9204	0.00621
64.0	179.0	0.4854	0.9310	0.00620
128.0	221.9	0.5984	0.9407	0.00617
256.0	265.0	0.7106	0.9497	0.00616
512.0	303.6	0.8108	0.9588	0.00622
1024.0	333.5	0.8861	0.9664	0.00627

TABLE VIII.

*Dichloroacetic Acid*.  $\mu_{\infty} = 388.6$  at  $25^{\circ}$ .

V.	$\mu_{\infty}$	$\alpha$ .	$\alpha$ .	K.
16.0	231.4	0.6337	0.8835	0.0535
32.0	273.2	0.7400	0.9009	0.0534
64.0	309.8	0.8318	0.9174	0.0540
128.0	338.7	0.9020	0.9319	0.0550

TABLE IX.

*Trichlorobutyric Acid*.  $\mu_{\infty} = 379.0$  at  $25^{\circ}$ .

V.	$\mu_{\infty}$	$\alpha$ .	$\alpha$ .	K.
23.6	308.8	0.8816	0.8861	0.1783
47.2	331.7	0.9149	0.9068	0.1720
77.26	343.9	0.9434	0.9195	0.1720
108.0	350.4	0.9566	0.9273	0.1800

A comparison of the numbers in column five at once shows that for each acid a constant value of  $K$  is obtained. The degree of dissociation in the case of cyanoacetic acid has been varied from 0.23 to 0.83, but the equation holds good exactly throughout this interval.

The applicability of the formula has also been demonstrated for the entire range of transition electrolytes, beginning with cyanoacetic acid, which borders on the type of electrolytes included in the third group, and ending with trichlorobutyric acid, the strength of which is comparable with that of mineral acids.

#### Summary.

The abnormally high mobility of the hydrogen and hydroxyl ions in aqueous solutions has been explained on the assumption that electricity is partly carried by the ordinary process of convection and partly propagated through water molecules undergoing alternate dissociation and recombination. The apparently high activity-coefficients of strong acids and bases in aqueous solutions

has also been traced to this cause. A modified Ostwald equation,  $\frac{(\alpha x)^2}{(1-x)V} = K$ , based on the consideration that only free ions have the capacity of regenerating undissociated molecules, has been developed for weaker electrolytes, where the degree of dissociation is less than one. It has been shown that this equation becomes identical with Ostwald's dilution law in the case of very weak electrolytes where  $\alpha$  is always very nearly equal to one, and also gives very concordant values for the equilibrium constant in the case of "transition electrolytes" where Ostwald's equation is not applicable.

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LXX.—*The Freezing Point Curve of Mixtures of Toluene-o- and -p-sulphonamides. Composition of Mixtures of Toluene-o- and -p-sulphonic Acids.*

By PHYLLIS VIOLET MCKIE.

AN accurate method of estimating the relative amounts of toluene-o- and -p-sulphonic acids in a mixture of the two acids can be based on the fusion curve of mixtures of the corresponding amides.

The composition of these acid mixtures has previously been investigated by Holleman (*Ber.*, 1911, **44**, 2504), by determining the freezing points of mixtures of the sulphonyl chlorides prepared from them. In this case, toluene-*m*-sulphonic acid was also generally present in small proportion. The freezing points of the *o*- and *p*-chlorides lie on a simple but rather flat eutectic curve. The eutectic point is not well defined, nor has it been directly determined by Holleman. From his figures, it would appear that this point lies in the neighbourhood of 1°, and that the eutectic mixture contains from 15 to 25 per cent. of the *p*-chloride.

The low range of temperature over which many of the mixtures of the *o*- and *p*-chlorides solidify (the *p*-chloride melts at 66.7° and the *o*-chloride at 10.0°, Holleman, *loc. cit.*), and the considerable manipulative difficulties encountered in preparing the mixture of chlorides in a state in which the fusion point can be observed (*loc. cit.*), constitute objections to the use of this method for the purpose

of determining the composition of mixtures of the toluene-*o*- and -*p*-sulphonic acids.

These difficulties are lessened or disappear if the mixture of crude acid chlorides is converted into amides, a transformation which can be very simply and quantitatively carried out. Moreover, it is necessary only to dry the amide mixture before determining the fusion point, whereas the mixture of acid chlorides must finally be distilled under diminished pressure. The melting points of the mixtures of amides lie in a very convenient range of temperature, namely, 110—156°, and, as will be seen from the curve, the eutectic point is extremely sharply defined. The eutectic mixture contains 61.25 per cent. of the *p*-sulphonamide, and melts at 110.25°.

*Preparation of Materials.*—The toluenesulphonic acid, or mixture of acids, is converted into the sulphonyl chloride by treatment with phosphorus pentachloride and phosphoryl chloride (Polak, *Rec. trav. chim.*, 1910, **29**, 416; compare Holleman, *loc. cit.*), and the sulphonyl chlorides are extracted with ether from the product of the reaction after it has been treated with ice. After some of the ether has been evaporated, solid ammonium carbonate, and finally some alcoholic ammonia, is added, the mixture being gently warmed by placing it at intervals on a water-bath. The reaction is known to be complete when the very penetrating odour of the sulphonyl chloride has disappeared. The conversion may also be conveniently effected by grinding the mixture in a mortar.

The product of amidation, after the evaporation of solvents, is extracted with as little cold water as possible to remove ammonium salts, and then dried at 100° to expel the water of crystallisation of the *p*-amide.

The *p*-amide separates from aqueous solution with two molecules of water. The dihydrate melts, if heated rapidly, at 105°, but is best rendered anhydrous by drying at 100°:

0.1730 when dried at 100—110° for two hours lost 0.0282.

$H_2O = 16.3$ .

$C_7H_9O_2NS \cdot 2H_2O$  requires  $H_2O = 17.3$  per cent.

Both the *o*- and *p*-amides can be purified and almost completely freed from the isomeride by careful crystallisation from water. Final purification was effected by sublimation in the vacuum of a Töpler pump, which raised the melting point by a few tenths of a degree. Resublimation of material which had been thus treated produced no further change.

The melting point of toluene-*p*-sulphonamide is given as 137° (Klason and Vallin, *Ber.*, 1873, **12**, 1853), and that of toluene-*o*-

sulphonamide as 153—154° (Wolkow, *Zeitsch. für Chem.*, 1870, 327) and 155° (Noyes, *Amer. Chem. J.*, 1886, 8, 176). After sublimation in a vacuum, the latter melts at 156·3° and the former at 137·45°.

*Determination of the Fusion Points.*—Holleman recommends a special form of heating-bath (*loc. cit.*), by means of which stirring is avoided. In the present work, the following arrangement was employed: The heating-bath is a beaker containing clear, colourless glycerol, and is fitted with a stirrer. The material is placed in a small tube, fitted with a thermometer reading to 0·1° and a stirrer. This tube is enclosed in a larger tube, so that an air-space prevents direct contact with the glycerol. Sufficient material is taken to ensure that the bulb of the thermometer is completely covered by the molten mass. With the thermometer and the tube which were used, 0·5—1·5 grams were required. The whole apparatus was carefully screened from draughts.

The heat was supplied by a small hooded gas-jet, regulated by a screw clip compressing the rubber tubing. No difficulty was experienced in keeping the temperature of the bath constant over considerable periods. When determining a melting point, the temperature of the bath was raised to within a degree or so of the expected fusion point *before* introducing the jacketed tube containing the material. Prolonged heating and sublimation were thus avoided. The inner tube with its fittings—thermometer and stirrer—and containing the material, was weighed before and after a determination in order to check any loss through sublimation. The maximum loss observed in any case amounted only to 0·0004 gram on a total weight—tube, thermometer, material, etc.—of 10 grams.

The temperature of the bath is gradually raised until incipient fusion is observed. At no time was the temperature of the heating-bath more than 1° above that registered by the thermometer in the material. The melting point is taken as the temperature at which the material liquefies, save for one or two crystals. On maintaining the thermometer steady for ten to fifteen minutes, the crystals should not disappear. On raising the temperature 0·1°, they should melt.

In the case of the pure substances, the variation of the thermometer from the point of incipient fusion to complete melting did not extend to more than 0·5°.

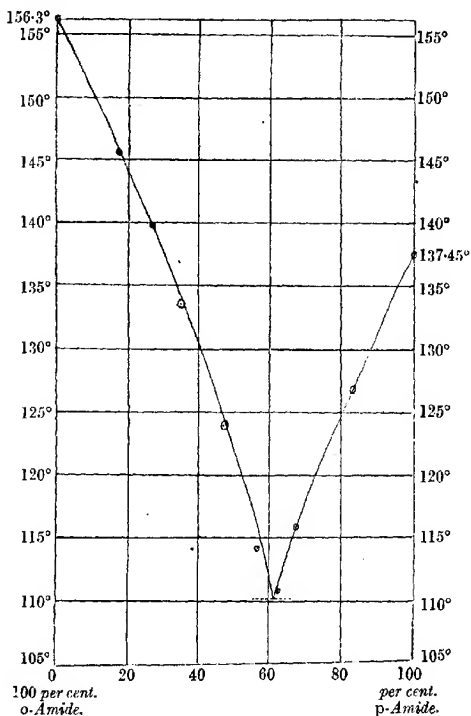
*Toluene-p-sulphonamide.*—Middle fraction of the sublimate obtained by sublimation in vacuum.

(1) Incipient fusion, 137°; bath, 138° for ten minutes. All but



one crystal melted,  $137.40^{\circ}$ ; bath,  $138^{\circ}$  for fourteen minutes. Last crystal melted,  $137.5^{\circ}$ .

(2) The temperature was kept at  $137.45^{\circ}$  for five minutes; all but one crystal melted. This melted on raising the temperature to  $137.5^{\circ}$ , bath  $138^{\circ}$ . The melting point of toluene-*p*-sulphonamide is therefore taken as  $137.45^{\circ}$ .



*Toluene-o-sulphonamide*.—The crude material has an average melting point of  $148$ – $152^{\circ}$ . One recrystallisation from water raises the melting point to  $154$ – $155^{\circ}$ . On further recrystallisation, the melting point is raised to  $156^{\circ}$ . Material which had been recrystallised from water was sublimed in a vacuum. As in the former case, all but the middle fraction was neglected.

(1) Incipient fusion,  $156.1^{\circ}$ ; bath,  $157^{\circ}$  for ten minutes. All

but one crystal melted,  $156.3^\circ$ ; bath,  $157^\circ$  for ten minutes. Last crystal melted,  $156.4^\circ$ .

(2) The external temperature was maintained at  $156.7^\circ$  for twenty minutes, the temperature of the inner thermometer registering  $156.3^\circ$ . A trace of solid remained, which melted on raising the temperature to  $156.4^\circ$ . The melting point of toluene-*o*-sulphonamide is therefore taken as  $156.3^\circ$ .

*Plotting of the Curve.*—The melting point of a weighed portion of one of the components was determined. Successive weighed portions of the other pure component were then added, and the melting point was determined for each mixture. The curve was followed, starting from both the pure ortho- and the pure para-compound. When the curve had been plotted in this way, single points on it were determined, separate mixtures being made up for each determination.

<i>o</i> -Amide. Gram.	<i>p</i> -Amide. Gram.	<i>p</i> -Amide. Per cent.	Melting point.
0.3241	0H	0	$156.3^\circ$
0.3241	0.0709	17.96	145.5
0.3958	0.1381	25.87	139.7
0.3235	0.1787	35.58	133.6
0.3958	0.2698	40.54	130.3
0.3235	0.2839	46.74	124.0
0.3958	0.4020	50.39	120.8
0.2478	0.3267	56.87	114.1
0.3958	0.6230	61.15	110.4
0.3958	0.8200	67.45	115.9
0.1212	0.5752	82.59	126.8
0.2839	0.0	100.0	137.45

I wish to express my thanks to Professor Orton, at whose suggestion and under whose direction this work has been carried out, for his guidance and criticism.

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## LXXI.—The Compound $H_2B_4O_6$ and its Salts.

By RAMES CHANDRA RAY.

In a previous communication (T., 1914, 105, 2162), it was shown that the so-called amorphous boron, prepared by the reduction of boron trioxide by means of magnesium, probably consisted of a solid solution of a lower oxide of boron, sometimes in combination with a little magnesium oxide, in elementary boron. If this were

really the case, it appeared probable that the soluble part of the fusion would contain some of the lower oxide, together with excess of boron trioxide, and the present investigation was undertaken with a view to detect and isolate the lower oxide.

The fusion obtained by heating a mixture of boron trioxide with magnesium powder generally contains magnesium boride, amorphous boron (so-called), magnesium oxide, partly in combination with boron trioxide, and, as will be shown later, the lower oxide or oxides of boron. If the operation is carried out under conditions which will now be described, the quantity of magnesium boride in the mixture is very small, although it cannot be altogether eliminated.

A mixture of 1 part of magnesium powder and 3.5 parts of anhydrous boron trioxide, finely powdered and passed through a 120-mesh sieve, was heated in a covered magnesia-lined crucible, through which a current of hydrogen was passed, to a bright red heat for about three hours. After cooling in an atmosphere of hydrogen, the mass was powdered and mixed with half its weight of anhydrous boron trioxide. The mixture was then heated again as before. The fused mass was powdered, water was added to it, and it was allowed to remain for from one to three days, to allow of the decomposition of traces of magnesium boride.

The solution was filtered, and the boric acid removed by the method employed by Travers, Ray, and Gupta (*Pamphlet*, H. K. Lewis and Co., 1916), which consisted in shaking the solution in a vacuum for several days with precipitated magnesium hydroxide, and removing the excess of the latter, together with the insoluble magnesium metaborate, by filtration. In analysing the solutions, advantage was also taken of the fact, discovered by Travers, Ray, and Gupta (*loc. cit.*), that when solutions of the lower oxides of boron are evaporated with excess of lime and the residue ignited to constant weight, oxidation does not take place and the increase in the weight of the lime corresponds with the weight of the lower oxide in the solution. For the purpose of analysis, three equal quantities of the solution were treated as follows:

(a) The magnesium was precipitated in the usual manner and the result expressed as the oxide  $MgO$ .

(b) The solution was introduced into a platinum crucible containing lime, ignited to constant weight, and, after evaporation to dryness, the crucible was again ignited to constant weight, the increase in weight giving the weight of the magnesium oxide and of the lower oxide of boron, together with the weight of any trace of boric acid left in the solution.

(c) The third portion of the solution was evaporated to dryness in a vacuum and the residue heated in a sealed bulb with concentrated nitric acid. The bulb became filled with red fumes, and the lower oxide of boron was oxidised to boron trioxide. The bulb was then opened, the excess of nitric acid removed by evaporation in a vacuum desiccator over solid sodium hydroxide, and the boric acid determined by the lime method.

The following are the results of the experiments:

	I.	II.	III.	IV.	V.
MgO per 100 c.c. of solution.....	0.0980	0.1156	0.1248	0.0876	0.1608
Residue less MgO per 100 c.c. ....	0.3048	0.3584	0.3896	0.2726	0.5012
$B_2O_3$ from residue per 100 c.c. ....	0.3452	0.4036	0.4324	0.3048	0.5684
MgO in gram-mols. per 100 c.c. ....	0.0024	0.0029	0.0031	0.0022	0.0040
B in gram-atoms per 100 c.c. ....	0.0099	0.0115	0.0123	0.0087	0.0161
Ratio B/Mg .....	4.1	3.9	4.1	3.9	4.0
$B_2O_3$ .....					
(Residue less MgO) } ...	1.132	1.126	1.112	1.118	1.130

It is clear that the ratio B/Mg is very near 4, and that the mean value of the ratio  $B_2O_3/(\text{Residue less MgO})$ , which is 1.124, closely approximates to the value of the ratio  $2B_2O_3/B_4O_6$ , which is 1.129. The analytical results appear, therefore, to suggest that the solution contains a magnesium borite, the formula of which may be written  $MgO.B_4O_6$ . The oxide  $B_4O_6$  has already been described by Travers, Ray, and Gupta (*loc. cit.*).

Each of the solutions used in these experiments was obtained from the treatment of a different fusion, and it was possible, therefore, although hardly probable, that the constancy of their composition might be attributable to the fact that the conditions in each case were similar. The third preparation was therefore treated with water four times, and the extracts were investigated separately. The results of the analysis of the first extract have already been given; those of the remaining extracts are tabulated below:

	III, a.	III, b.	III, c.
MgO per 100 c.c. ....	0.0960	0.0616	0.0412
Residue less MgO per 100 c.c....	0.2940	0.1804	0.1212
$B_2O_3$ from residue per 100 c.c....	0.3290	0.1996	0.1368
MgO in gram-mols. ....	0.0024	0.0015	0.0010
B in gram-atoms .....	0.0094	0.0057	0.0039
Ratio B/Mg .....	3.9	3.8	3.9
$B_2O_3$ .....			
(Residue less MgO) } .....	1.119	1.106	1.128

Although the solutions became more and more dilute with each treatment of the fusion with water, their composition remained

practically constant, leaving no room for doubt that the compound  $MgO.B_4O_5$  is really present in them.

It has not been found possible to isolate the magnesium borite.

The molecular weight of the compound can be determined with sufficient accuracy from the freezing points of the solutions. If the magnesium salt were completely dissociated, the molecular weight of the corresponding oxide could be determined from the formula

$$\Delta = 18.5(W/M + W'/40),$$

where  $W$  is the weight, in 100 c.c. of the solution, of the oxide of boron,  $M$  its molecular weight, and  $W'$  the weight of the magnesium oxide present. Since, however, the compound is probably dissociated only to the extent of about 75 per cent., the result will be about 15 per cent. too high.

For the determination of the freezing points, measured quantities of the solutions, of which the analyses have already been given, were evaporated to dryness in a vacuum. The residues were dissolved in a measured quantity of water, and the freezing points were compared with the freezing point of pure water. The following results were obtained:

	I.	II.	III.	IV.	V.
$W$ .....	0.3048	0.3584	0.3896	0.2726	0.5012
$W'$ .....	0.0980	0.1156	0.1248	0.0876	0.1608
$\Delta$ .....	0.090	0.105	0.115	0.082	0.148
$M$ .....	121	128	125	124	125
Ratio $B_4O_5/MgO$ .....	1.0	0.95	1.0	1.0	1.0

The values for  $M$  agree sufficiently well with the theoretical value, 124, as calculated for the formula  $B_4O_5$ .

On addition of ammonia to the solution, the magnesium is almost completely precipitated as hydroxide, and if the ammoniacal solution is evaporated in a vacuum, a residue is left which consists mainly of the oxide. As Travers, Ray, and Gupta have shown (*loc. cit.*), the oxide is very unstable and is readily oxidised to boric acid.

If a solution of the magnesium salt is treated with potassium hydroxide in equivalent proportions, and afterwards evaporated in a vacuum to small bulk, practically the whole of the magnesium separates as hydroxide and can be filtered off. On further concentration of the solution in a vacuum, the potassium salt separates as a crust which can be redissolved, and the salt purified by crystallisation five or six times, and finally dried in a vacuum at  $80-90^\circ$ . The preparation is a difficult one, and altogether only 2 to 3 grams

of the substance were finally obtained. The salt is stable in the absence of moisture.

The potassium was estimated by first dissolving the salt in water, evaporating the solution to dryness in a platinum vessel, and treating the residue repeatedly with hydrochloric acid and methyl alcohol. The potassium chloride was finally converted into sulphate. For the estimation of boric acid, the solution was saturated with carbon dioxide and boiled under a reflux condenser in a current of pure air. The boric acid was titrated with *N*/20-alkali in the presence of mannitol, using phenolphthalein as indicator:

- I. 0.5036 gave 0.3987  $K_2SO_4$  and 0.3142  $B_2O_3$ .  $K=35.5$ ;  
 $B=19.6$ .
- II. 0.2286 gave 0.1821  $K_2SO_4$  and 0.1433  $B_2O_3$ .  $K=35.7$ ;  
 $B=19.7$ .
- III. 0.3678 gave 0.2889  $K_2SO_4$  and 0.2318  $B_2O_3$ .  $K=35.2$ ;  
 $B=19.8$ .

$K_2B_4O_6$  requires  $K=35.8$ ;  $B=20.2$  per cent.

The analyses are concordant, and the results in agreement with the values corresponding with the formula  $K_2B_4O_6$ , which may therefore be accepted as correct.

The molecular weight of the substance was determined by the cryoscopic method, using 20 grams of solvent:

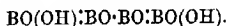
0.0435 gave  $\Delta t = -0.052$ . M.W. = 78.

0.0874 „  $\Delta t = 0.097$ . M.W. = 84.

The value of the molecular weight calculated for the formula  $K_2B_4O_6$  is 218, and if the compound were completely dissociated in solution, the apparent molecular weight would be 73. The concentrations of the two solutions correspond with 1 gram-equivalent in 100 and 50 litres respectively, and if the salt is ionised to the same extent as similar potassium salts, the degree of ionisation in the two solutions will be approximately 0.9 and 0.8. Without going further into the matter, it is obvious that, within the limits of experimental error, the result proves that the substance in solution has the formula  $K_2B_4O_6$ , and not the formula  $KB_2O_3$ , which would dissociate into two ions and give an apparent molecular weight of approximately 50.

The existence of the anhydrous salt,  $K_2B_4O_6$ , of the acid  $H_2B_4O_6$  is of interest, as it goes to confirm the views put forward by Travers, Ray, and Gupta (*loc. cit.*) as to the constitution of the borohydrates containing four atoms of boron. If the boron atoms in these compounds are linked in a single chain, the oxide,  $B_4O_3$ ,

which can be obtained by heating them; must be given the formula  $\text{BO}:\text{BO}:\text{BO}:\text{BO}$   
 $\text{——O——}$ , and the corresponding acid the formula



The results do not offer any positive evidence that the so-called amorphous boron is a solid solution of the oxide  $\text{B}_4\text{O}_7$  in elementary boron, particularly as Travers, Ray, and Gupta have found indications of the existence of the oxide  $\text{B}_2\text{O}_3$ , which is quite insoluble in water, and may be the oxide that is present in the solid solution. The research has, however, led to the discovery of a new series of compounds, the acid,  $\text{H}_2\text{B}_4\text{O}_7$ , and its salts, and the results serve to extend our knowledge of the more complex compounds of boron.

In conclusion, I desire to thank Dr. M. W. Travers, F.R.S., at whose suggestion the research was undertaken, for the valuable help which I have always received from him.

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## LXXII.—*The Hydrates and Alcoholate of Calcium Benzoate.*

By FREDERICK STANBRIDGE.

THE investigations recorded in this paper were suggested by a chance observation by Dr. C. F. Baker of the action of alcohol on calcium benzoate. This salt, in its usual form, is a crystalline trihydrate having the formula  $\text{Ca}(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2\cdot 3\text{H}_2\text{O}$ . When heated on the water-bath, it loses part of its water, and it was noticed that when this partly dehydrated substance was covered with alcohol, a distinct change in appearance took place, the substance becoming flocculent.

Close examination under the microscope of the action of alcohol on the trihydrate showed the presence, a minute after adding the alcohol, of nuclei on each crystal from which, as centres, bundles of new, needle-shaped crystals grew with great rapidity. Similar results were obtained in tests made under the microscope on the completely dehydrated salt, obtained by heating the trihydrate in an air-oven, in which the original crystalline shape was retained in spite of the loss of water.

These observations point to the formation of a compound of calcium benzoate and alcohol, formed from the anhydrous substance by the simple addition of alcohol, and from the trihydrate by the substitution of alcohol for the water of crystallisation. This compound was prepared and analysed.

The calcium benzoate was prepared specially from pure benzoic acid and pure precipitated calcium carbonate by the usual method. The average yield of the trihydrate from 40 grams of benzoic acid was: first crop, 34 grams; second crop, 11 grams; third crop, 4 grams, a total of 49 grams, representing 89 per cent. of the theoretical yield, which is 55.1 grams. The purity of the salt was checked by estimations of the water and of the calcium. (Found:  $H_2O=15.80$ ,  $15.74$ ;  $Ca=14.15$ ,  $14.12$ . Calc.:  $H_2O=16.08$ ;  $Ca=14.21$  per cent.)

The new compound was prepared by first dehydrating 10 grams of the trihydrate in the air-oven at about  $150^\circ$ , allowing to cool, and then adding 30 c.c. of alcohol specially dried by distillation from quicklime. The mixture became warm and set to a soft mass. It was allowed to remain for a day, being stirred a few times to break up lumps. The excess of alcohol was removed by filtration, and the solid product pressed between filter-paper. After drying in the air, analysis showed that the substance had reverted almost completely to the trihydrate. (Found:  $H_2O=15.99$  per cent.) In order to ensure drying, and yet to prevent the elimination of combined alcohol, it was found satisfactory to place the product over a mixture of anhydrous calcium chloride and alcohol for four days.

The dried material is a light, white powder having a strong odour of alcohol. Under the microscope, it was seen to consist of very small, transparent needles which, on the addition of a drop of water, clotted together in semi-opaque masses, with needle-shaped crystals projecting from their boundaries. On gently heating a small portion of the substance in a test-tube, alcohol was given off copiously, and this condensed to liquid in the upper, cooler part of the tube. With sodium carbonate and iodine solutions the substance gave the iodoform reaction for alcohol.

In order to determine the exact proportions of alcohol and water in combination in the product, the matter volatile up to  $150^\circ$  was estimated by combustion. A sample was weighed in a small U-tube, and then this was half immersed in a beaker of sulphuric acid provided with a thermometer and stirrer. The temperature of the bath was raised to  $150^\circ$ , while a stream of pure and dry air was passed through the U-tube and thence through a combustion tube filled with copper oxide and heated in a furnace. The



water and carbon dioxide were absorbed and weighed as usual, and from the weights of these the quantities of water and alcohol in the sample were calculated. Analyses at intervals gave the following results, after correction by a blank experiment:

Time after placing over calcium chloride and alcohol.	Water, per cent.	Alcohol, per cent.
4 days .....	0.51	24.36
5 " .....	0.11	24.68
7 " .....	2.03	24.46
17 " .....	—	24.02
494 " .....	2.03	21.61
$\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot 2\text{C}_2\text{H}_5\text{O}$ requires .....	0	24.61

The results leave no doubt that the substance is a dialcoholate of calcium benzoate, having the formula  $\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot 2\text{C}_2\text{H}_5\text{O}$ . Calcium benzoate thus shows a property which is shared by a number of other salts of calcium, of taking up alcohol to form an unstable additive compound.

The next question that presented itself was, What happens when the trihydrate is treated with alcohol? As alcohol is hygroscopic, it should extract water from the trihydrate, but whether a lower hydrate, the anhydrous salt, or the alcoholate is to be expected as the result cannot be stated without further investigation as to the compounds possible and the conditions under which these are stable.

Rough experiments, made by adding different mixtures of alcohol and water to the trihydrate, to ascertain between what limits of composition action took place at the ordinary temperature, showed that a mixture containing 95 per cent. of alcohol by volume had no action, whilst one containing 97 per cent. acted rapidly.

Attempts to determine by a dilatometer the temperature at which a given mixture of alcohol and water just begins to act on the trihydrate met with no success, but using the thermometric method with the same mixture of alcohol and water ( $D^{15.6}$  0.8149, corresponding with 92.85 per cent. of alcohol by weight), a marked change was observed to take place at  $35.5^\circ$ , the trihydrate being transformed into silky, oblong plates. After separating these and drying them over a mixture of calcium chloride and alcohol for one to two days, analyses were carried out in the same way as in the case of the alcoholate:

Found:  $\text{H}_2\text{O} = 6.43, 6.42$ ;  $\text{C}_2\text{H}_5\text{O} = 0$ .

$\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 6.00$  per cent.

The new substance is therefore the monohydrate formed from the trihydrate by the extraction of 2 molecules of water of crystallisation by the mixture of alcohol and water.

Since another hydrate of calcium benzoate besides the ordinary one had thus been found, it was decided to make a study of calcium benzoate by itself to see what possible substances might be formed by the action of alcohol on the trihydrate.

In order to search for transition points, a dilatometer was first used, containing trihydrate and anhydrous substance and filled with amyl alcohol in one set of experiments, and containing trihydrate and monohydrate and filled with toluene in another set. Beyond slight evidence of a transition point below  $90^{\circ}$  in the second set of experiments, no very definite results were obtained.

The measurement of the solubility of the trihydrate at various temperatures was adopted finally as the best method. The apparatus used was similar to that described by Lumsden (T., 1902, 81, 350), employing, however, a hot-air motor for stirring the thermostat tank, an electro-motor for stirring the mixture of crystals and water, and a mercury thermo-regulator of the Ostwald pattern. A gas-pressure regulator of the form A described by Stansfield (*Trans. Faraday Soc.*, 1911, 7, 116) was employed, by which the temperature in the thermostat tank could be kept constant within  $0.1^{\circ}$  quite easily, even at the highest temperature,  $97^{\circ}$ , at which the tank was used. After placing the solubility apparatus in position in the tank, the mixture of crystals and water was stirred for periods varying from  $4\frac{1}{2}$  to  $12\frac{1}{2}$  hours. The mixture was then filtered into a receiver while the whole apparatus was still immersed. At first a small flask was used as receiver, and from this about 10 c.c. of the solution were transferred to a weighed platinum crucible for analysis. For determinations at  $80^{\circ}$  and upwards, the flask was replaced by a weighing bottle, into which the solution was filtered directly in order to obviate, as far as possible, loss of water by evaporation during the transference of the hot solution, and, after weighing, the solution was poured into a platinum basin for analysis. This apparatus and procedure sufficed for temperatures from about  $20^{\circ}$  up to  $97^{\circ}$ . For  $10^{\circ}$ , the temperature of the tank was adjusted by passing a stream of ice-cold water through the zig-zag tube provided for the purpose on the bottom of the tank. For  $0^{\circ}$ , the same saturation and filtration apparatus was immersed in clean, chopped ice. For determinations at the boiling point of the saturated solution, at first the Beckmann ebullioscopic apparatus was employed. Excess of the powdered crystals was boiled with distilled water in the apparatus for about three hours, and the temperature and barometric height were noted. Some of the solution was then drawn by suction into a weighing bottle through a tube to the lower end of which was attached a small glass bulb filled with cotton wool in order to

retain any solid. The sample was weighed and transferred to a platinum basin for analysis. The boiling point of pure water was determined in the same apparatus under the same conditions, the barometric height being again noted. From the latter observation, the correction to be added to the observed temperature of the boiling solution to get the true temperature was obtained, and from this the elevation of the boiling point of the saturated solution above that of pure water. Later it was found simpler to boil excess of the powdered crystals with water in an ordinary boiling tube with a layer of beads at the bottom and with a small reflux condenser at the top, the barometric height during the course of the experiment being noted. The temperature of the boiling solution was obtained indirectly by adding to the boiling point of pure water at the observed pressure, as given by tables, the mean elevation of the boiling point by saturation with the crystals as determined by the first experiments with the Beckmann apparatus.

In all cases, in order to estimate the strength of the saturated solution, this was evaporated to dryness, the residue repeatedly treated with concentrated sulphuric acid and ignited, and the calcium weighed as calcium sulphate.

When  $90^{\circ}$  was passed, results were obtained which appeared anomalous, but this was soon found to be due to the existence of a transition point between  $80^{\circ}$  and  $90^{\circ}$ . Special care was taken in this interval of temperature, and the solubility was measured at about  $83^{\circ}$ ,  $85^{\circ}$ ,  $87^{\circ}$ , and  $89^{\circ}$ , whereby it was ascertained that the transition point is near  $85^{\circ}$ , and that the solubility curve above this temperature is distinct from that below. It was possible to obtain points on the metastable portions of both curves near  $85^{\circ}$  which enabled them to be plotted, and therefore the transition point to be ascertained with greater accuracy. The change from the hydrate stable at the lower temperatures to that stable at the higher temperatures is so sluggish at  $90^{\circ}$  that three of the ordinary solubility determinations, lasting for seven or eight hours, for which the mixture of crystals and water was heated to  $90^{\circ}$ , but not above, gave points on the curve for lower temperatures. For the same reason, to get the points for  $85^{\circ}$ ,  $87^{\circ}$ ,  $89^{\circ}$ ,  $91^{\circ}$ , and  $93^{\circ}$  on the curve for higher temperatures, it was found necessary to heat the mixture to  $98^{\circ}$  before the period of saturation. To obtain results for  $83^{\circ}$  on the metastable portion of the curve for higher temperatures, it was found satisfactory to mix calcium benzoate, completely dehydrated, with a hot solution saturated at the boiling point, and to cut down the time of mixing and stirring at  $83^{\circ}$  to about two hours.

All results which were not obviously untrustworthy are collected

in table I. Each was obtained from a separate complete experiment, unless indicated otherwise by brackets. The temperatures have been corrected, and are probably true to  $0.1^{\circ}$ . The solubility is expressed as grams of anhydrous calcium benzoate per 100 grams of water. The hydrate that is in contact with the saturated solution is denoted by the figure I for that stable at lower temperatures and II for that stable at higher temperatures.

TABLE I.

Temperature.	Solubility.	Hydrate.	Temperature.	Solubility.	Hydrate.
0-2°	2-235	I	84.9°	7-652	II
0-2	2-229	"	87-0	7-702	"
0-2	2-232	"	87-0	7-705	"
9-8	2-454	"	87-0	7-718	"
9-8	2-452	"	89-1	7-832	"
19-9	2-720	"	89-1	7-870	"
19-9	2-726	"	89-1	7-848	"
19-9	2-722	"	89-1	7-852	"
29-8	3-016	"	90-3	8-614	I metastable
30-1	3-026	"	90-2	8-529	" "
39-7 }	3-426	"	90-2	8-523	" "
39-7 }	3-421	"	91-1	8-040	II
39-7	3-426	"	91-1	7-949	"
49-7	4-070	"	91-1	8-026	"
49-7 }	4-032	"	93-2	8-237	"
49-7 }	4-056	"	93-1	8-198	"
49-7	4-036	"	93-2	8-087	"
59-8	4-719	"	93-1	8-095	"
59-8	4-699	"	95-2	8-349	"
59-8	4-708	"	95-2	8-371	"
69-7	5-630	"	95-2	8-424	"
69-9	5-618	"	96-2	8-371	"
69-7	5-710	"	97-2	8-450	"
70-0	5-769	"	97-2	8-453	"
70-0	5-650	"	97-2	8-539	"
79-6	6-857	"	97-2	8-513	"
79-9	6-865	"	100-2	8-800	"
82-9	7-561	II metastable	99-6	8-537	"
82-9	7-502	" "	100-0	8-455	"
82-9	7-518	" "	99-4	8-610	"
82-9	7-528	" "	99-5	8-766	"
84-9	7-614	II	100-6	8-880	"
85-0	7-563	"	100-4	8-814	"

Many efforts were made to obtain specimens of the solid hydrate stable in contact with saturated solution above the transition point. The first method used was that described by Lumsden (*loc. cit.*), the apparatus employed being similar to that figured by him. No results of any value were obtained; the solid product was a fine white powder, and consequently retained a considerable quantity of saturated solution. By the second method, two small quantities of the trihydrate were heated in separate small bulbs in communication with one another to temperatures above the

transition point, but one somewhat higher than the other, whereby the water in the saturated solution formed in the first was made to distil gently over into the second until no further loss of weight of the first bulb and contents could be detected. In two experiments of this kind there was a loss of 30.22 grams and 30.48 grams of water per gram-molecule of the trihydrate in the hotter bulb, suggesting the formation of the monohydrate, for which the loss of weight per gram-molecule of the trihydrate would be 36 grams.

It appeared desirable to complete the study of the equilibrium of solutions of calcium benzoate in water by determining the freezing-point curve of solutions of various strengths. The measurements of the freezing points were carried out in the usual manner with the Beckmann apparatus. The experiments were made in two series, in the first of which successive quantities of powdered trihydrate were added to a given quantity of water in the apparatus, whereas in the second a stock solution of calcium benzoate was made, slightly more concentrated than the solution saturated at 0°, and the freezing points of this and of solutions consisting of 80, 60, 40, and 20 c.c. of the stock solution diluted to 100 c.c. with water, were determined. The results of the two series of experiments are given in table II.

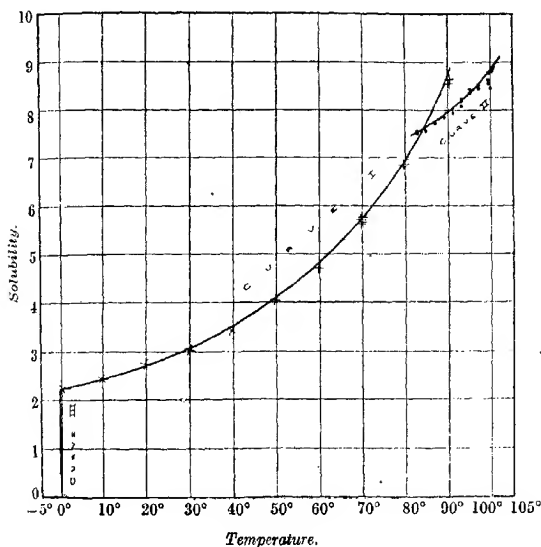
TABLE II.

1st Series.		2nd Series.	
Grams of $\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2$ per 100 grams of water.	Freezing point.	Grams of $\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2$ per 100 grams of water.	Freezing point.
0	0°	0	0°
0.3098	-0.100	0.4473	-0.129
0.7880	-0.220	0.8964	-0.159
1.421	-0.308	1.347	-0.282
1.760	-0.370	1.801	-0.289
—	—	2.263	-0.332
—	—	3.470	-0.369

The mean graphs for the two sets of determinations do not coincide very nearly, but by taking points midway between them along the ordinates, it is possible to make, for a given quantity of calcium benzoate in solution, an approximation to the freezing point correct to about 0.01°. The cryohydric point was about -0.37°.

The results in tables I and II are shown in the diagram, which represents completely the stable equilibrium between calcium benzoate and its solutions at all temperatures between the cryohydric point and the boiling point of the saturated solution. The

solubility curve consists of two distinct portions, the one (I) for the lower temperatures defining equilibrium between the trihydrate and saturated solution, the other (II) for the higher temperatures defining that between a lower hydrate and saturated solution. The two curves cross at  $84.7^{\circ}$ , corresponding with a concentration of 7.62 grams of calcium benzoate per 100 grams of water, and this is therefore the transition point. Curve III is the freezing-point curve, and the concentration at the cryohydric point  $-0.37^{\circ}$ , obtained by extrapolation of curves I and III, is



2.22 grams of calcium benzoate per 100 grams of water. As regards the solid phases, that corresponding with curve I is undoubtedly the trihydrate. Although it has not been possible to isolate from the saturated solution that corresponding with curve II, there is reason for supposing it to be the monohydrate,  $\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ .

#### Summary.

Anhydrous calcium benzoate combines with alcohol to form a dialcoholate,  $\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot 2\text{C}_2\text{H}_5\text{O}$ , which is very unstable.

Mixtures of alcohol and water containing much alcohol extract

water from the crystalline trihydrate,  $\text{Ca}(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2\cdot 3\text{H}_2\text{O}$ , to form a monohydrate,  $\text{Ca}(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2\cdot\text{H}_2\text{O}$ .

A study of the solubility of the trihydrate at various temperatures shows that a lower hydrate exists, the transition temperature being  $84.7^\circ$  and the solubility 7.62 grams of calcium benzoate per 100 grams of water. This lower hydrate is probably the monohydrate,  $\text{Ca}(\text{C}_6\text{H}_5\cdot\text{CO}_2)_2\cdot\text{H}_2\text{O}$ .

A study of the freezing points of solutions of calcium benzoate shows that the cryohydric point is  $-0.37^\circ$ , when the solution contains 2.22 grams of calcium benzoate per 100 grams of water.

The action of mixtures of alcohol and water on hydrates should furnish some interesting examples of equilibria in systems of three components with one liquid and two or more solid phases, but the author has refrained from introducing into the present example any theoretical speculations based on the phase rule without further experimental work.

In conclusion, the author desires to record his grateful appreciation of the sympathetic interest taken by Dr. C. F. Baker in the course of the work.

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### LXXIII.—N-Acyl Derivatives of Carbazole.

By MAURICE COPISAROW.

IN the course of certain investigations, it was found necessary to prepare N(9)-acyl derivatives of carbazole.

As but few substances of this class are known,\* it was decided to investigate this subject further, this being the more desirable, as the known methods of preparation are not satisfactory.

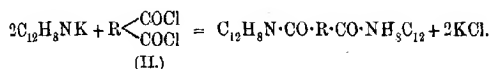
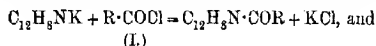
The drawbacks of the methods so far employed are: (1) The necessity of heating the acid chloride or anhydride with carbazole

\* N-Acetylcarbazole (Graebe and Glaser, *Annalen*, 1872, 163, 351; Böeseken, *Rec. trav. chim.*, 1912, 31, 164), carbazole-N-carboxylic acid (Giamician and Silber, *Gazzetta*, 1882, 12, 272; Odde, *ibid.*, 1911, 41, I., 255), N-benzoylcarbazole (Bizzarri, *ibid.*, 1890, 20, 413; Mazzara, *Ber.*, 1891, 24, 279), and carbazole-N-carbonyl-o-benzoic acid (Stümmer, *Monatsh.*, 1907, 28, 411).

to a comparatively high temperature before the reaction takes place, the product being impure and the yield low; (2) the employment of condensing agents, such as sulphuric acid, ferric chloride (Bösesken, *loc. cit.*), and aluminium chloride (Stümmer, *loc. cit.*; Scholl and Neovius, *Ber.*, 1911, **44**, 1249), which may cause the formation of *C*-acyl derivatives of carbazole (Borsche and Feise, *Ber.*, 1907, **40**, 378); and (3) the constitution of the carbazole derivatives so formed is established only in an indirect or negative manner.

The author has found that by adopting in this case a method analogous to that generally employed in the preparation of *N*-alkyl derivatives of carbazole, namely, condensing the acid haloids, usually the chlorides, with potassium carbazole, good results are obtained.

The general mechanism of formation of the *N*-acyl derivatives of carbazole can be represented by the following equations:



It was observed that the energy of reaction and the stability of the products decrease with the complexity of the acyl group in the case of monobasic acids.

It has also been noted that in the case of the *C*- and *N*-acyl derivatives of carbazole, their solubility and fusibility diminish with the increase in the number of carbazole groups in the molecular structure of the product (Stümmer, *loc. cit.*; Scholl and Neovius, *loc. cit.*; Ehrenreich, *Monatsh.*, 1911, **32**, 1102; Copisarow and Weizmann, *T.*, 1915, **107**, 878).

The *N*-acyl derivatives of carbazole investigated by the author give colourless solutions in concentrated sulphuric acid, these solutions assuming a deep green coloration on the addition of a few drops of concentrated nitric acid, the only exception being *N*-oxalylcarbazole. This is probably due to the greater stability of oxalylcarbazole, on the one hand, and the comparative ease with which the derivatives containing one carbazole group in their molecule are hydrolysed, regenerating carbazole, on the other. So far as the experimental evidence goes, *N*-oxalylcarbazole cannot be regarded as an intermediate product in the formation of "carbazole-blue," prepared by the fusion of carbazole with oxalic acid (Suida, *Ber.*, 1879, **12**, 1403; Bamberger and Müller, *ibid.*, 1887, **20**, 1903).

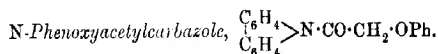


## EXPERIMENTAL.

The general method of preparation of the *N*-acyl derivatives of carbazole adopted by the author was to triturate potassium carbazole, prepared by Graebe's process (*Annalen*, 1880, **202**, 28), with a slight excess of the acid chloride; the reaction being energetic, the addition of the latter is regulated accordingly. The mixture is allowed to remain for two hours, then extracted successively with water, dilute sodium carbonate, and water again, so as to remove the potassium chloride and acidic substances, and then dried.

On triturating potassium carbazole with acetyl and benzoyl chlorides, there were obtained the *N*-acetyl and *N*-benzoyl derivatives of carbazole respectively, in the forms described by previous workers (*loc. cit.*).

The following compounds are further examples of the general reaction.

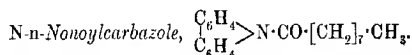


The product of the interaction of potassium carbazole and phenoxyacetyl chloride, a pale grey powder, is soluble in all the ordinary organic solvents. It crystallises from ethyl alcohol (after decolorising the solution with animal charcoal) in white, slender needles decomposing at 121—122°, with the regeneration of carbazole.

The colourless solution of *N*-phenoxyacetylcarbazole in concentrated sulphuric acid gives with nitric acid the deep green coloration characteristic of carbazole:

0.3854 gave 15.16 c.c.  $\text{N}_2$  at 18° and 763 mm.  $\text{N} = 4.59$ .

$\text{C}_{20}\text{H}_{15}\text{O}_2\text{N}$  requires  $\text{N} = 4.62$  per cent.

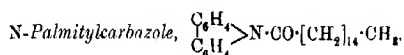


The product of the reaction of potassium carbazole with *n*-nonoyl chloride is readily soluble in the usual organic solvents. It crystallised from ethyl alcohol in long, prismatic needles melting at 72—73°:

0.3266 gave 12.4 c.c.  $\text{N}_2$  at 17° and 762 mm.  $\text{N} = 4.42$ .

$\text{C}_{21}\text{H}_{25}\text{ON}$  requires  $\text{N} = 4.56$  per cent.

On heating *N*-*n*-nonoylcarbazole above its melting point, the acyl group is eliminated, decomposition also taking place on attempting to crystallise the substance from a solvent of high boiling point.



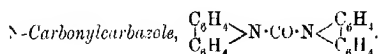
The reaction between potassium carbazole and palmityl chloride, being less energetic than those described above, is completed by keeping the mixture in an air-oven at  $75^\circ$  for two hours, the mixture being triturated from time to time.

The product, a grey powder, is readily soluble in all the ordinary organic solvents. The difference in solubility in hot and in cold ethyl alcohol is considerable, and the compound crystallises from this solvent in a spongy mass of small, white, matted needles melting at  $90-91^\circ$ . It separates from benzene in small, rhombic crystals:

0.4603 gave 12.4 c.c.  $\text{N}_2$  at  $18^\circ$  and 763 mm.  $\text{N} = 3.12$ .

$\text{C}_{28}\text{H}_{30}\text{ON}$  requires  $\text{N} = 3.45$  per cent.

On being heated above its melting point, the compound decomposes, carbazole being regenerated.



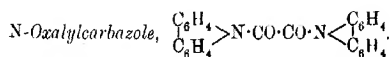
Dry carbonyl chloride was passed over finely powdered potassium carbazole, the current of gas being so regulated as to keep the temperature of the energetic reaction at  $150-160^\circ$ . When the reaction ceased, the product, freed from potassium chloride and acidic substances, was crystallised from ethyl alcohol, the first crop of crystals being mainly unchanged carbazole. After three crystallisations, the compound was obtained in small, white needles melting at  $181-183^\circ$ :

0.2805 gave 19 c.c.  $\text{N}_2$  at  $16^\circ$  and 760 mm.  $\text{N} = 7.92$ .

$\text{C}_{25}\text{H}_{16}\text{ON}_2$  requires  $\text{N} = 7.78$  per cent.

N-Carbonylcarbazole is more readily soluble than carbazole in the ordinary organic solvents.

Paschkowitzky's (*Ber.*, 1891, **24**, 2905) failure to prepare N-carbonylcarbazole by boiling potassium carbazole with carbonyl chloride in benzene solution was probably due to the low temperature. Even in boiling xylene no condensation takes place, although the reaction appears to be energetic.



The reaction between potassium carbazole and oxalyl chloride is energetic, and the operation was carried out in a manner similar

to that adopted in the case of monobasic acid derivatives of carbazole. Under these conditions, no acid of the type  $>\text{N}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  was formed. The crude product, freed from potassium chloride and oxalic acid, was extracted with hot alcohol to remove any unaltered carbazole. The pale grey powder is very sparingly soluble in alcohol, ether, light petroleum, chloroform, or pyridine, but somewhat more readily so in ethyl acetate, acetic acid, benzene, nitrobenzene, acetone, or carbon disulphide, and crystallises from nitrobenzene or carbon disulphide in small, white, rhombic crystals melting at  $265\text{--}266^\circ$ :

0.2360 gave 14.56 c.c.  $\text{N}_2$  at  $17^\circ$  and 762 mm.  $\text{N}=7.18$ .

$\text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{N}=7.21$  per cent.

*N*-Oxalylcarbazole does not give with concentrated nitric acid in the presence of concentrated sulphuric acid the deep green coloration characteristic of carbazole and many of its derivatives.

It appeared to be of interest to investigate whether this substance is an intermediate product in the formation of "carbazole-blue" from carbazole and oxalic acid. To determine this, the following experiments were carried out: (1) The product of the reaction between oxalyl chloride and potassium carbazole was heated to above  $200^\circ$ ; (2) the product of the reaction between oxalyl chloride and carbazole was heated to above  $200^\circ$ ; and (3) oxalylcarbazole was fused with a large excess of oxalic acid and the mixture heated to above  $200^\circ$ .

In all these cases, no formation of "carbazole-blue" could be detected, and therefore *N*-oxalylcarbazole cannot be regarded as an intermediate product in the formation of "carbazole-blue."

The author wishes to express his indebtedness to the Department of Industrial and Scientific Research for permission to publish this work.

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## Organic Chemistry.

**Synthesis of  $\alpha$ - $\delta$ -Heptanetriol, True Homologue of Ordinary Glycerol, and of some Derivatives of Propyltetrahydrofuran.** J. HAMONET (*Ann. Chim.*, 1918, [ix], 10, 5—30).—In part a more detailed account of work already published (compare A., 1916, i, 246). When  $\alpha$ - $\gamma$ -dimethoxyheptan- $\delta$ -ol is acted on by phosphorus tri-iodide, it yields methyl iodide and 2- $\gamma$ -methoxypropyltetrahydrofuran, b. p. 190—192°,  $D_{20}^{25}$  0.9559,  $n_D^{20}$  1.440, and not the required iododimethoxyheptane. Similar attempts to prepare the corresponding bromo-compound were not successful, but  $\delta$ -chloro- $\alpha$ - $\gamma$ -dimethoxyheptane, b. p. 120—122°/16 mm., was obtained by the action of phosphorus trichloride.  $\alpha$ - $\gamma$ -Dibromoheptan- $\delta$ -ol (*loc. cit.*), when distilled, decomposed, giving 2- $\gamma$ -bromopropyltetrahydrofuran, b. p. 115—116°/27 mm.,  $D_{20}^{25}$  1.331,  $n_D^{20}$  1.485. W. G.

**Preparation of certain Alkylating Reagents.** JAMES COLQUHOUN IRVINE and WALTER NORMAN HAWORTH (Brit. Pat. 117824, 1918).—In the interaction of sulphuryl chloride and methyl or ethyl alcohol, the formation of an alkyl chlorosulphonate and alkyl sulphate have been observed (Behrend, A., 1877, i, 182; ii, 287), but under suitable conditions the main product is a mixture of alkyl sulphate and alkyl hydrogen sulphate. On distillation under diminished pressure, the alkyl hydrogen sulphate in the mixture undergoes decomposition into sulphuric acid and alkyl sulphate, so that a good yield of the latter is obtained. The sulphuryl chloride may be preformed or may be prepared *in situ* from sulphur dioxide and chlorine. [See also *J. Soc. Chem. Ind.*, 1906A.] D. F. T.

**Kephalin. V. Hydrokephalin of the Egg-yolk.** P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1918, 35, 285—290. Compare this vol., i, 93).—Hydrokephalin has been isolated in an almost pure state from the sample of hydrolecithin previously suspected of containing it (*loc. cit.*). The raw material was freed from unsaturated compounds by dissolving in chloroform and then pouring into a large excess of ether. It was then subjected to repeated fractional crystallisation from a mixture of equal volumes of chloroform and ethyl methyl ketone, and then from a mixture of chloroform and alcohol (1:2). The final preparation had the correct empirical composition,  $C_{41}H_{82}O_8NP$ , corresponding with the structure  $C_{17}H_{35}CO \cdot O \cdot CH < \begin{matrix} CH_2 \cdot O \cdot CO \cdot C_4H_9 \\ CH_2 \cdot O \cdot PO(OH) \cdot O \cdot CH_2 \cdot CH_2 \cdot NH_2 \end{matrix}$ , which may therefore be regarded as established for the substance. The rotation of the pure substance is  $[\alpha]_D^{25}$  in chloroform +6.0°.

H. W. B.

**Manufacture of Ethylidene Diacetate.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 112766, 1918).—Ethylidene acetate is prepared by passing acetylene into a solution of mercuric oxide in glacial acetic acid to which an alkyl sulphate, particularly methylene sulphate, has also been added. [See also *J. Soc. Chem. Ind.*, 606A.] D. F. T.

**The Acid Function in the Methenic and Methinic Derivatives.** J. GUINCHANT (*Ann. Chim.*, 1918, [ix], 9, 49—108; 109—143; 1918, [ix], 10, 30—84).—A more detailed account of work already published (compare A., 1895, i, 649; 1896, i, 594; ii, 12, 465). W. G.

**Reduction of Aldehydes to Corresponding Alcohols. I. Reduction of Heptaldehyde.** P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1918, 35, 281—283).—The method is essentially the same as that employed for the reduction of esters (Levene and Allen, A., 1917, i, 3). An emulsion of metallic sodium in toluene is first prepared, and a solution of the aldehyde in glacial acetic acid and toluene is slowly added, the mixture being continuously cooled and stirred. The yield is about 60% of the theoretical. *Hepyl phenylcarbamate*,  $C_{14}H_{23}O_2N$ , prepared by heating the alcohol with an equal weight of phenylcarbimide at  $175^\circ$  for a few minutes, crystallises from dilute alcohol in needles, m. p.  $60^\circ$  (corr.). H. W. B.

**Effect of Variations in the Available Alkali on the Yield of Acetone in the Oxidation of Butyric Acid with Hydrogen Peroxide.** EDGAR J. WITZEMANN (*J. Biol. Chem.*, 1918, 35, 83—100).—When butyric acid is oxidised by means of hydrogen peroxide in dilute solution in the presence of variable amounts of alkali hydroxide, the quantity of acetone recoverable is greatest when the reaction of the system is neutral to faintly acid. As the alkalinity increases, the velocity of oxidation of the butyric acid also increases, but the yield of acetone decreases probably because the acetone itself becomes increasingly susceptible to oxidation with the increasing alkalinity. When dextrose is added to the reaction mixture, the products of oxidation of the dextrose reduce the alkalinity if the supply of alkali is limited, resulting in an increased production of acetone. If, however, there is an excess of alkali, the dextrose exerts a "sparing" action on the butyric acid which is analogous to the "sparing effect" of carbohydrate in the body. H. W. B.

**isoPhorone.** MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], 23, 219—224. Compare A., 1911, i, 939, and following abstracts).—The author has prepared and purified, as far as possible, by distillation a large quantity of isophorone, and from it has obtained two oximes, one having m. p.  $70$ — $73^\circ$  and the other m. p.  $97$ — $100^\circ$ . When boiled with alcoholic potassium hydroxide, the oxime, m. p.  $73^\circ$ , is slowly converted into its isomeride. Only one semicarbazone, m. p.  $187^\circ$ , was obtained. W. G.

**Homophorone.** MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], **23**, 224—229. Compare A., 1911, i, 939, and preceding and succeeding abstracts).—From the fraction 160—200° obtained in the fractionation of crude isophorone, homophorone,  $C_6H_{10}O$ , has been isolated as a colourless liquid, b. p. 192—194°, giving only one oxime, m. p. 87—88°, which, unlike those from isophorone, is easily decomposed by hydrochloric acid, but is not transformed into an isomeride by potassium hydroxide. Homophorone semicarbazone has m. p. 206°.

W. G.

**Action of Dilute Sulphuric Acid on Pure Pinacone.**

MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], **23**, 229—232. Compare preceding abstracts).—A theoretical discussion of work already published (compare A., 1911, i, 347, 939).

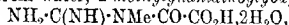
W. G.

**The Conversion of Lævulose diphosphoric Acid into the corresponding Monophosphoric Acid.**

CARL NEUBERG (*Biochem. Zeitsch.*, 1918, **88**, 432—436).—This conversion can be brought about by gentle warming of a salt with *N*-hydrochloric acid or oxalic acid. The calcium salt of the monophosphoric acid has the formula  $C_6H_{11}O_6PCa.H_2O$ , and the barium salt  $C_6H_{11}O_6P.Ba.H_2O$ . The monophosphate can be fermented by living yeast, whereas the diphosphate cannot.

S. B. S.

**Oxidation Product of Creatine.** LOUIS BAUMANN and HORSTEN INGVALDSEN (*J. Biol. Chem.*, 1918, **35**, 277—280).—After the removal of carnosine from an aqueous extract of muscle by means of mercuric acetate and sodium carbonate, a glistening, laky substance is gradually precipitated from the filtrate. By decomposition of the precipitate with hydrogen sulphide and re-crystallisation from water, *α-methylguanidinoglyoxylic acid*,



is obtained in the form of glistening flakes, m. p. 203—204°. The new compound is evidently produced from creatine by the oxidising action of mercuric acetate, and can also be prepared directly by the oxidation of either pure creatine or creatinine. It is somewhat toxic, 0.15 gram injected into a guinea-pig causing death in two hours. Its injection into a dog increases the elimination of creatine in the urine.

H. W. B.

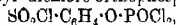
**Hypochlorous, Hypobromous, and Hypoiodous Amides.**

ÉTIENNE BOISMENU (*Ann. Chim.*, 1918, [ix], **9**, 144—188).—A résumé of work already published (compare A., 1911, i, 957; 1912, i, 15, 97).

W. G.

**Action of the Chlorides of Phosphorus on Phenolphonic Acids. II.**

RICHARD ANSCHÜTZ and EUGEN MOLINEUS (*Annalen*, 1918, **415**, 51—64. Compare A., 1908, i, 83).—Chlorosulphonylphenyl dichloro-orthophosphate,



is converted by heating with an equimolecular quantity of phosphorus pentachloride at  $180^{\circ}$  into *p*-chlorophenyl dichloro-orthophosphate, and the latter, treated similarly at  $250^{\circ}$ , is converted quantitatively into *p*-dichlorobenzene. *p*-Chlorosulphonylphenyl metaphosphate,  $\text{SO}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}_3$ , obtained by heating the corresponding dichloride with the calculated quantity of water (weighed in the form of anhydrous oxalic acid), forms transparent crystals and is converted into *p*-chlorosulphonylphenyl dihydrogen phosphate by exposure to moisture in the air.

Potassium *p*-acetoxybenzenesulphonate,  $\text{SO}_3\text{K}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ , crystals, prepared by heating potassium phenol-*p*-sulphonate with acetic anhydride at  $150^{\circ}$ , is converted by phosphorus pentachloride on the water-bath into *p*-acetoxybenzenesulphonyl chloride, crystals, m. p.  $78^{\circ}$ , b. p.  $148^{\circ}/12$  mm., which reacts in ethereal solution with aniline, *p*-toluidine, and piperidine (2 mols.) to form the anilide,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHPh}$ , m. p.  $126$ — $127^{\circ}$ , *p*-toluidide, m. p.  $98$ — $99^{\circ}$ , and piperidide, m. p.  $115$ — $116^{\circ}$ , respectively. These three substances are converted by heating with alcohol (the first requires potassium hydroxide in addition) into phenol-*p*-sulphonanilide, needles, m. p.  $137$ — $138^{\circ}$ , *p*-toluidide, needles, m. p.  $151$ — $152^{\circ}$ , and *p*-piperidide, m. p.  $132$ — $133^{\circ}$ , respectively.

When heated with carbon tetrachloride and phosphorus pentachloride at  $180$ — $200^{\circ}$ , 2:6-dibromo-4-chlorosulphonylphenyl dichloro-orthophosphate (*loc. cit.*) is converted into 4-chloro-3:5-dibromobenzenesulphonyl chloride,  $\text{C}_6\text{H}_2\text{ClBr}_2\cdot\text{SO}_2\text{Cl}$ , crystals, m. p.  $94$ — $5^{\circ}$ , b. p.  $203$ — $208^{\circ}$ , and this is converted into 1:2:4:6-tetrachlorobenzene by phosphorus pentachloride at  $200^{\circ}$ . C. S.

**Sulphonylides.** RICHARD ANSCHÜTZ (*Annalen*, 1918, 415, 64—97. Compare A., 1912, i, 852).—[With (FRL.) CLARA ZYMANDL.]—*o*-Chlorosulphonylphenyl dichloro-orthophosphate,  $\text{SO}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{POCl}_2$ ,

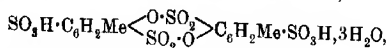
yellow oil, b. p.  $185^{\circ}$ , obtained from sodium phenol-*o*-sulphonate and phosphorus pentachloride (rather more than 1 m.), is converted by heating with phosphorus pentachloride at  $250^{\circ}$  into *o*-chlorophenyl dichloro-orthophosphate, pale yellow oil, b. p.  $135$ — $137^{\circ}/12$  mm., which yields *o*-chlorophenol by boiling with water, and *o*-dichlorobenzene by heating with phosphorus pentachloride at  $250^{\circ}$ .

Sodium acetoxybenzene-*o*-sulphonate,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ , obtained by heating the phenol-*o*-sulphonate with acetic anhydride, is converted by phosphorus pentachloride into acetoxybenzene-*o*-sulphonyl chloride, colourless crystals, m. p.  $73\cdot2$ — $73\cdot9^{\circ}$ , which yields the sulphonanilide,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHPh}$ , m. p.  $106$ — $107^{\circ}$ , and sulphon-*p*-toluidide, leaflets, m. p.  $116$ — $117^{\circ}$ , by treatment with aniline and *p*-toluidine respectively; these are hydrolysed, the latter by boiling alcohol alone, the former by the calculated quantity of boiling alcoholic potassium hydroxide, yielding phenol-*o*-sulphonanilide,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHPh}$ , leaflets, m. p.  $126\cdot5$ — $127\cdot5^{\circ}$ , and phenol-*o*-sulphon-*p*-toluidide, leaflets, m. p.  $124$ — $125^{\circ}$ .

each of which develops a violet coloration with alcoholic ferric chloride. Phenylene-*o*-sulphonyl chloride is produced when an ethereal solution of acetoxybenzene-*o*-sulphonyl chloride is treated with gaseous ammonia or with an ethereal solution of diethylamine, acetyl chloride being eliminated.

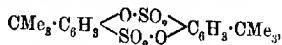
[With L. HODENIUS.]—Sodium 4-acetoxytoluene-3-sulphonate, prepared from the *p*-cresolsulphonate and acetic anhydride at 150°, is converted by phosphorus pentachloride into 4-acetoxytoluene-3-sulphonyl chloride, m. p. 55–56°, b. p. 165–170°/20 mm., which yields tolylene-3:4-sulphonyl chloride by treatment with ethereal ammonia or diethylamine. The following three compounds are prepared by methods similar to the preceding: sodium 4-acetoxytoluene-3:5-disulphonate, 4-acetoxytoluene-3:5-disulphonyl chloride, crystals, m. p. 115°, and 4-acetoxytoluene-3:5-disulphonyldiethylamide,  $\text{OAc} \cdot \text{C}_6\text{H}_4\text{Me}(\text{SO}_2 \cdot \text{NET}_2)_2$ , crystals, m. p. 150°.

Tolylene-3:4-sulphonyl chloride-5:5'-disulphonic acid,



is prepared by treating *p*-cresol-3:5-disulphonic acid with fuming sulphuric acid (60%  $\text{SO}_3$ ), finally at 100° with the further addition of the fuming acid, and recrystallising the precipitate from dilute nitric acid; it forms a potassium salt, long needles with  $5\frac{1}{2}\text{H}_2\text{O}$ , silver salt, colourless needles, and ferric salt, colourless needles, and, when anhydrous, reacts with phosphorus pentachloride to form tolylene-3:4-sulphonyl chloride-5:5'-disulphonyl chloride, crystals, decomp. about 280°, which is stable to boiling water.

1:4-tert.-Butylphenol-3-sulphonic acid,  $\text{CMe}_3 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{SO}_3\text{H}$ , is obtained by heating *p*-tert.-butylphenol with pure sulphuric acid at 70–80°. Its sodium salt, anhydrous crystals, yields by acetylation sodium 4-acetoxy-1-tert.-butylbenzene-3-sulphonate, which is converted by phosphorus pentachloride on the water-bath into 4-acetoxy-1-tert.-butylbenzene-3-sulphonyl chloride, crystals, m. p. 103°. tert.-Butylphenylene-3:4-sulphonyl chloride,



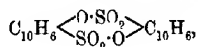
microscopic needles, m. p. 301–302°, is obtained by the action of phosphoryl chloride on 1:4-tert.-butylphenol-3-sulphonic acid. The following amyl compounds are prepared like the corresponding butyl compounds: 1:4-tert.-amylphenol-3-sulphonic acid and its sodium salt, sodium 4-acetoxy-1-tert.-amylbenzene-3-sulphonate, 4-acetoxy-1-tert.-amylbenzene-3-sulphonyl chloride, b. p. 142–146°/4 mm., and tert.-amylphenylene-3:4-sulphonyl chloride, colourless crystals, m. p. 228–229°.

The substance obtained by Schiff (*Annalen*, 1875, 178, 187) by heating sulphotannic acid or its acetyl derivative with acetic anhydride is 5:6-diacetoxy-*o*-phenylenesulphonyl chloride.

[With (FRL.) MARIA MAXIM.]—Sodium 2-acetoxynaphthalene-1-sulphonate, faintly red needles, prepared by acetylating the



naphtholsulphonate, is converted by phosphorus pentachloride in the presence of chloroform into 2-acetoxynaphthalene-1-sulphonyl chloride, crystals, m. p. 115.5°, which cannot be converted into a sulphonylide by means of pyridine, neither can 2-naphthol-1-sulphonyl chloride, colourless needles, m. p. 124°, obtained by hydrolysing the preceding acetyl derivative with warm dilute sodium hydroxide. The following derivatives of 1-naphthol-2-sulphonic acid are obtained by methods similar to the preceding: potassium 1-acetoxynaphthalene-2-sulphonate, colourless prisms, 1-acetoxynaphthalene-2-sulphonyl chloride, crystalline powder, m. p. 87.5°, 1-acetoxynaphthalene-2-sulphonamide, stout, yellow needles without a sharp m. p., and the corresponding sulphonanilide,  $\text{OAc}\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NHPH}$ , crystals, m. p. 157.5°, and sulphon-p-toluidide, m. p. 135.5°. 2:1-Naphthylenesulphonylide,



colourless, crystalline powder, decomp. above 300°, is obtained (1) by adding phosphoryl chloride with cooling to a mixture of potassium 1-naphthol-2-sulphonate, pyridine, and chloroform, (2) by shaking 1-acetoxynaphthalene-2-sulphonyl chloride with pyridine at the ordinary temperature.

Sodium 2-naphthol-1-sulphonate yields 2-naphthol-1:3:6:7-tetrasulphonic acid by heating with four parts of fuming sulphuric acid (40%  $\text{SO}_3$ ) at 120–130° for eight hours, but when heated with five parts for two days is converted into a substance, colourless crystals, which appears to be 3:2-naphthylenesulphonylide-1:6:7:1':6':7'-hecasulphonic acid (sodium salt,  $\text{C}_{20}\text{H}_8\text{O}_{24}\text{S}_6\text{Na}_6$ , colourless, prismatic needles).

Acetylisethionyl chloride,  $\text{OAc}\cdot\text{CH}_3\cdot\text{CH}_2\cdot\text{SO}_2\text{Cl}$ , b. p. 130–132°/14 mm., obtained, together with  $\beta$ -chloroethylsulphonyl chloride by heating potassium acetylisethionate with phosphorus pentachloride on the water-bath, cannot be converted into diethylenesulphonylide by means of ammonia or diethylamine; the sulphonylide also cannot be prepared from isethionic acid and phosphoric oxide or phosphoryl chloride. C. S.

**The Stereochemistry of Quinquevalent Nitrogen. VI.** SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 151–159).—After reviewing the state of knowledge with respect to the decomposition of quaternary ammonium compounds by heat and the various proposals for the representation of the spatial distribution of the valencies of the quinquevalent nitrogen atom, the author agrees with the assumption that four of the valencies possess the same value, whilst the fifth is of a different nature and suggests an extension of the views of Meisenheimer (A., 1909, i. 20; 1912, i. 25; 1913, i, 595) on the structure of the quinquevalent nitrogen atom. The atom is regarded as situate at the centre of a tetrahedron, at the corners of which the four radicles are disposed; the fifth and negative radicle is in an outer zone, and occupies a fixed

position which, however, may vary with the manner of formation of the ammonium compound, thus influencing the optical rotation of the substance, but leaving the chemical properties unaffected. By this hypothesis, the existence of two modifications of *d*-phenylbenzylmethylallylammonium iodide (Komatsu, A., 1915, i, 1054) is explained.

D. F. T.

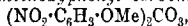
**The Solidifying and Boiling Points of Phenol and the Cresols.** J. J. FOX and M. F. BARKER (*J. Soc. Chem. Ind.*, 1918, 37, 268—272 $\pi$ ).—The authors have determined the freezing-point and boiling-point curves of mixtures of phenol, and *o*-, *m*-, and *p*-cresols taken in pairs. Phenol and *o*-cresol show a continuous freezing-point curve with a minimum corresponding nearly with equimolecular proportions, but no eutectic point. The boiling-point curve is nearly a straight line. The phenol-*m*-cresol freezing-point curve has two minimum (eutectic) points, and between them a maximum at 17°, indicating the formation of a molecular compound of the formula  $C_6H_5\cdot OH, 2C_7H_7\cdot OH$ . The compound forms a eutectic with phenol at 10.2° and with *m*-cresol at -4°. The boiling-point curve is a normal binary mixture curve. The freezing-point curve for phenol and *p*-cresol shows a sharp eutectic with equimolecular proportions of the constituents, whilst the boiling-point curve is normal.

When the cresols are taken in pairs, those containing *m*-cresol show the most complicated curves. The freezing-point curve of *m*- and *p*-cresols shows a maximum at 20% *p*-cresol, but only one eutectic, a 50% mixture, was detected. The curve for *o*- and *m*-cresols shows two distinct breaks, but no maximum, and the existence of a compound cannot be inferred.

The results show that many different mixtures of phenol and the cresols have the same freezing point. It is unsafe to consider a sample of "cresylic acid" free from phenol because it yields a distillate which does not freeze when immersed in ice-water.

E. H. R.

**Nitro-derivatives of Guaiacol.** FANNY POLLECOFF and ROBERT ROBINSON (T., 1918, 113, 645—656).—The nitration of 4-nitroguaiacol yields 4:6-dinitroguaiacol, and of 4-nitroguaiacyl acetate a mixture of the 3:4- and the 4:5-dinitro-derivatives in undetermined proportions. By nitration, guaiacol carbonate yields successively 5-nitro-2-methoxyphenyl carbonate,



colourless needles, m. p. 133°, and 3:5-dinitro-2-methoxyphenyl carbonate, colourless needles, m. p. 148°, which yield on hydrolysis 5-nitroguaiacol and 3:5-dinitroguaiacol, pale yellow needles, m. p. 40°, respectively. The nitration of 5-nitroguaiacol yields 5:6-dinitroguaiacol, yellow prisms, m. p. 205—208° (decomp.) (acetate, colourless needles, m. p. 124—125°), together with the 4:5-isomeride as by-product; the former, after reduction and treatment with phenanthraquinone, yields 1-hydroxy-2-methoxyphenanthra-

*phenazine*, golden-yellow needles, m. p. 224°. 4:5-Dinitroguaiacol forms pale yellow needles, m. p. 172° (acetate, colourless, prismatic needles, m. p. 123—124°, sintering at 114°), and is converted as above into 2-hydroxy-3-methoxyphenanthraphenazine, yellow threads, m. p. 239—240°.

The further nitration of 4:6-, 5:6-, or 4:5-dinitroguaiacol is not practicable, but the 3:5-isomeride readily yields 3:5:6-trinitroguaiacol, yellow prisms, m. p. 129° (decomp.), as the sole product, which forms a characteristic pyridine salt,  $C_7H_5O_6N_3 \cdot C_5H_5N$ , yellow needles, m. p. 180°, 185°, or 194—195° (decomp.; according to the rate of heating), and yields 3:5:6-trinitroveratrole, pale yellow needles, m. p. 174°, by methylation. The last compound is converted into 3:5-dinitro-2:6-diaminoanisole, garnet needles, m. p. 237°, by boiling methyl-alcoholic aqueous ammonia, and into 4:6-dinitro-1:2:3-trimethoxybenzene, pale yellow needles, m. p. 85°, by boiling methyl-alcoholic potassium hydroxide. C. S.

**Synthesis of Elemicin and of isoElemicin.** F. MAUTHNER (*Annalen*, 1917, **414**, 250—255).—2:6-Dimethoxyphenyl allyl ether,  $C_6H_3(OMe)_2 \cdot O \cdot CH_2 \cdot CH:CH_2$ , a colourless oil, b. p. 140—141°/14 mm., prepared from allyl bromide and pyrogallol 2:6-dimethyl ether in boiling acetone in the presence of potassium carbonate, is converted by heating at 220° in a few minutes into 2:6-dimethoxy-4-allylphenol,  $OH \cdot C_6H_2(OMe)_2 \cdot CH_2 \cdot CH:CH_2$ , b. p. 168—169°/11 mm., which yields by methylation with methyl sulphate and 10% sodium hydroxide solution 3:4:5-trimethoxy-allylbenzene, identical with elemicin. The position of the allyl group is proved by oxidising the substance in acetone to gallic acid trimethyl ether by potassium permanganate, and of the double linking by the decomposition of the ozonide by water, whereby homogallaldehyde trimethyl ether is obtained. By heating with alcoholic potassium hydroxide, the synthetic elemicin is converted into isoelemicin (3:4:5-trimethoxypropenylbenzene), the ozonide of which yields gallaldehyde trimethyl ether by decomposition with water. [See *J. Soc. Chem. Ind.*, October.] C. S.

**Synthesis by means of Sodamide.** VIII. Phenyl-di-methylethyl Alcohol, Benzyl-, *o*-, *m*-, and *p*-Methylbenzyl- and *p*-Methoxybenzyl-dimethylethyl Alcohols. ALBIN HALLER and EDOUARD BAUER (*Ann. Chim.*, 1918, [ix], **9**, 5—24).—A résumé of work already published (compare A., 1911, i, 726; 1913, i, 168, 488; 1914, i, 418). W. G.

**Terpenes and Etheral Oils.** CXXI. Pulegenic Acid and the Conversion of Carvone into Pulegenic Acid. O. WALLACH (*Annalen*, 1917, **414**, 233—243).—An improved method of preparing pulegenic acid is to shake pulegone dibromide with aqueous potassium hydroxide for one hour at the ordinary temperature, and then for three hours at 100°. Unchanged pulegone and methylcyclohexanone are removed by steam, and pulegenic acid is

extracted by ether from the somewhat concentrated, acidified residual solution.

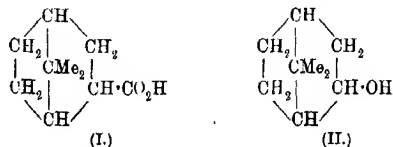
Like other substances containing a semicyclic linking, pulegenic acid,  $\text{CMe}_2\text{C} \begin{array}{c} \text{CH}(\text{CO}_2\text{H}) \\ \text{CH}_2 \end{array} \text{CHMe}$  (and also its amide), is difficult

to reduce to the saturated acid, which, however, can be obtained as follows: hydrogen chloride is added on to methyl pulegenate, and then removed again with simultaneous hydrolysis. The product is a mixture of ordinary pulegenic acid and an isomeride. By distillation under ordinary pressure, the former is converted into pulegene, whilst the latter distils at  $256\text{--}260^\circ$  with slight decomposition. It is converted into its amide, m. p.  $152^\circ$ , which is reduced easily by hydrogen and colloidal palladium to dihydropulegenamide, m. p.  $150\text{--}151^\circ$  (Eykmann gives  $147^\circ$ ), from which dihydropulegenic (1-methyl-3-isopropylcyclopentane-2-carboxylic) acid, b. p.  $139^\circ/12\text{ mm.}$ ,  $D^{24}_D 0.9600$ ,  $n_D 1.4524$ , is readily obtained. An alternative and more convenient method is to heat methyl hydrochloropulegenate with aniline, to reduce the resulting unsaturated ester by Skita's method, and to hydrolyse the product.

Dihydropulegenamide is converted by Hofmann's method into a base, presumably 2-amino-1-methyl-3-isopropylcyclopentane, which forms an acetyl derivative,  $\text{C}_{11}\text{H}_{21}\text{ON}$ , m. p.  $132^\circ$ , and a carbamide,  $\text{C}_{10}\text{H}_{20}\text{ON}_2$ , m. p.  $190^\circ$ .

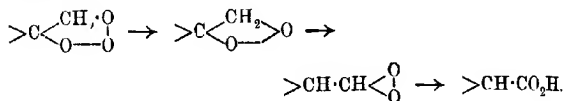
[With WOLFGANG VON RECHENBERG.]—The conversion of the 6-ring in carvone into the 5-ring of pulegenic acid, and the formation of this acid from dihydrocarvenolic acid, have been effected as follows. Dihydrocarvenolide, prepared from *d*-carvone, is hydrolysed by potassium hydroxide and boiling amyl alcohol, and the resulting dihydrocarvenolic acid, m. p.  $87^\circ$ , is converted by methylalcoholic hydrogen chloride at  $0^\circ$  into a saturated, chlorinated ester, m. p.  $15\text{--}16^\circ$ , b. p.  $114^\circ/12\text{ mm.}$ , which yields pulegenic acid, b. p.  $142\text{--}145^\circ/11\text{ mm.}$ ,  $D^{20}_D 0.9975$ ,  $n_D 1.4747$ ,  $[\alpha]^{20}_D +32.67^\circ$  in ether, by boiling with alcoholic sodium methoxide and subsequent hydrolysis. The pulegenic acid thus obtained is converted into its amide, m. p.  $152^\circ$  (occasionally  $123^\circ$ ; conditions of formation unknown), which yields dihydropulegenamide, m. p.  $150\text{--}151^\circ$ , by reduction as above. C. S.

**Total Synthesis of  $\alpha$ -Fenchenylic Acid (alloapo-Camphanecarboxylic Acid), and a New Type of Decomposition of Ozonides.** GUST. KOMPPA and R. H. ROSCHER (*Ann. Acad. Sci. Fennicae, A.*, [x], 18, 1—7; from *Chem. Zentr.*, 1918, i. 623—624).—In the ozonisation of  $\alpha$ -fenchene (Komppa and



x\*

Hintikka, A., 1914, i, 557; Komppa and Roschier, A., 1917, i, 466), the authors have obtained  $\alpha$ -fenchocamphorone and fenchenylic acid (annexed formula, I). The constitution of the latter is now confirmed by a synthesis of the acid from *dl*- $\alpha$ -fenchocamphorone, which, on reduction with sodium and alcohol, yields *dl*- $\alpha$ -fenchocamphorol (annexed formula, II), needles, m. p. 122—124°, b. p. 203°; from this, by conversion into the corresponding *dl*- $\alpha$ -fenchocamphoryl chloride,  $C_{10}H_{15}Cl$ , m. p. approx. 24—25°, b. p. 74·5°/13 mm., an organo-magnesium compound is obtainable which reacts with carbon dioxide, with formation of *dl*- $\alpha$ -fenchenylic acid (*allo*pocamphanecarboxylic acid). This result proves that the decomposition of the ozonide of  $\alpha$ -fenchene does not entirely follow the normal course, but that to some extent decomposition occurs without scission of a carbon atom, possibly as indicated by the scheme:



D. F. T.

**Action of Nitrous Acid on Methyl *p*-Dimethylaminobenzoate and *p*-Dimethylaminobenzaldehyde.** (Reactions of *tert.*-Amines, and a Contribution to the Subject of Steric Hindrance). FRANZ KLAUS and OSKAR BAUDISCH (*Ber.*, 1918, 51, 1036—1048. Compare A., 1907, i, 131).—When methyl *p*-dimethylaminobenzoate is treated with sodium nitrite and hydrochloric acid at  $-5^\circ$ , it yields methyl 3-nitro-4-dimethylaminobenzoate, m. p. 75° (Reverdin and Delétra, A., 1906, i, 273), and methyl *p*-nitrosomethylaminobenzoate,  $CO_2Me \cdot C_6H_4 \cdot NMe_2 \cdot NO$ , which crystallises in satiny needles, m. p. 115·5°. The identity of the latter compound is established by its reactions (A) and synthesis (B). A.—It yields *p*-nitrosomethylaminobenzoic acid, m. p. 202° on hydrolysis with sodium hydroxide; it gives *p*-methylaminobenzoic acid, m. p. 163°, and its methyl ester, m. p. 95·5° (not 73—75°, as Johnston stated, P., 1905, 156), when boiled with aqueous and methyl-alcoholic hydrochloric acid, respectively. B.—Methyl *p*-methylaminobenzoate is prepared by esterifying the acid or by hydrolysing *p*-nitrosomethylaminobenzoic acid with methyl-alcoholic hydrogen chloride, and is treated with nitrous acid, or methyl anthranilate is methylated by means of methyl sulphate and then nitrosated.

*p*-Dimethylaminobenzaldehyde behaves in a similar manner towards nitrous acid, the products being *p*-nitrosomethylaminobenzaldehyde,  $CHO \cdot C_6H_4 \cdot NMe_2 \cdot NO$ , pale straw-yellow crystals, m. p. 78°, 3-nitro-4-dimethylaminobenzaldehyde, m. p. 105°, and *p*-nitrosodimethylaniline. J. C. W.

**Amino-oxides.** OSKAR BAUDISCH (*Ber.*, 1918, 51, 1048—1058).—The action of permonosulphuric acid on *p*-dimethylaminobenzoic

acid leads to the formation of the sulphate of an amino-oxide. The free amino-oxide can be obtained by precipitation with potassium acetate, and it is found to give a number of characteristic salts, presumably of the oxonium type, and to behave in an interesting manner towards nitrous and sulphurous acids.

*p*-Dimethylaminobenzoic acid *N*-oxide,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{O}$ , crystallises in very long, prismatic needles, m. p.  $192\cdot5^\circ$ , gives formaldehyde when heated, and yields the following salts: *sulphate*, feathery groups of needles, as much as an inch long, with  $1\text{H}_2\text{O}$ , m. p.  $160^\circ$  (decomp.); *hydrochloride*, snow-white needles, m. p.  $184^\circ$ ; *aurechloride*, reddish-yellow, m. p.  $136^\circ$ ; *picrate*, yellow needles, m. p.  $155^\circ$ ; *platinichloride*, pink needles, m. p.  $155\text{--}156^\circ$ ; *ferrocyanide*, white needles. When a solution of the sulphate is saturated with sulphur dioxide, it suddenly becomes green and deposits white crystals of 4-dimethylamino-3-sulphobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{NMe}_2)\cdot\text{SO}_3\text{H}$ , m. p.  $279\text{--}280^\circ$ , the mother liquor containing *p*-dimethylaminobenzoic acid. A solution in dilute hydrochloric acid, when treated with sodium nitrite, yields some *p*-nitrodimethylaniline, a trace of *p*-nitrosodimethylaniline, but chiefly 3-nitro-4-dimethylaminobenzoic acid (A., 1907, i, 132). This has been reduced by means of stannous chloride to 3-amino-4-dimethylaminobenzoic acid, which crystallises in pale pink leaflets, m. p.  $152\text{--}153^\circ$ , and forms a *hydrochloride*, long needles, m. p.  $237^\circ$ , solutions of which give a deep red coloration and crystalline precipitate when warmed with ferric chloride.

*p*-Diethylaminobenzoic acid *N*-oxide has been prepared in a similar manner. It crystallises in long needles, m. p.  $170\text{--}171^\circ$ , evolves acetaldehyde on heating, and yields the following salts: *sulphate*,  $1\text{H}_2\text{O}$ , long, white needles, m. p.  $173\cdot5\text{--}174\cdot5^\circ$ ; *hydrochloride*, m. p.  $162\cdot5\text{--}163\cdot5^\circ$ ; *platinichloride*, m. p.  $178^\circ$ ; *aurechloride*, m. p.  $177^\circ$ ; *picrate*, m. p.  $169\text{--}171^\circ$ ; and *hydrogen ferrocyanide*, snowy leaflets. Sulphurous acid reduces it to *p*-diethylaminobenzoic acid and 4-diethylamino-3-sulphobenzoic acid, m. p.  $308\text{--}310^\circ$ , and nitrous acid converts it into a mixture of *p*-nitrosoethyl-aniline, *p*-nitrosoethylaminobenzoic acid, 3-nitro-4-ethylaminobenzoic acid, 3-nitro-4-diethylaminobenzoic acid, and *p*-nitrodiethyl-aniline.

J. C. W.

**isoValeric Acid, and its Abnormal Behaviour in the Perkin Synthesis.** ALFRED SCHAAERSCHMIDT, E. GEORGEACOPOL and JOHANN HERZENBERG (*Ber.*, 1918, 51, 1059—1074).—When *isovaleric* acid is applied to aldehydes under the conditions of the Perkin reaction, the main products are not the expected unsaturated acids, but the ethylenes derived from these by loss of carbon dioxide. The condensations take place at unusually low temperatures, so low, in fact, that it is doubtful if the unsaturated acids represent an intermediate stage at all. The authors believe that the primary  $\alpha$ -hydroxy-acid first loses carbon dioxide and then water rather than suffer decomposition in the reverse order.

The results of the experiments described are summarised as

follows, the weights, in grams, being given in brackets: Benzaldehyde (15), isovaleric anhydride (50), sodium isovalerate (45), heated for thirty hours at 100°, gave  $\alpha$ -isopropylcinnamic acid,  $\text{CHPh:CHPr}^\beta\text{:CO}_2\text{H}$  (1.9), leaflets, m. p. 118.5°, and  $\alpha$ -phenyl- $\gamma$ -methyl- $\Delta$ -butene,  $\text{CHPh:CHPr}^\beta$  (9.3). The same reagents, in the proportions 50:175:150, heated for six hours at 150°, gave the same hydrocarbon (46) (Schramm, A., 1883, 1094; Kunckell, A., 1904, i, 386; Klages, *ibid.*, 569). Benzaldehyde (15), acetic anhydride (55), and sodium isovalerate (45), heated for thirty hours at 100°, gave the same hydrocarbon (0.6), but no acid. Benzaldehyde (15), isovaleric anhydride (55), and sodium acetate (45), heated for ten hours at 150°, gave the hydrocarbon (3.2) and ordinary cinnamic acid (11).

Furfuraldehyde (50), isovaleric anhydride (150), and sodium isovalerate, heated for five hours at 150°, gave  $\alpha$ -2-furyl- $\gamma$ -methyl- $\Delta$ -butene,  $\text{C}_4\text{H}_3\text{O:CH:CHPr}^\beta$  (32), a pleasant-smelling, pale yellow oil, b. p. 64–66°/13 mm., 165–167°/atm., and a trace of  $\beta$ -2-furyl- $\alpha$ -isopropylacrylic acid,  $\text{C}_4\text{H}_3\text{O:CH:CHPr}^\beta\text{:CO}_2\text{H}$  (0.5), colourless leaflets, m. p. 114°. Furfuraldehyde (25), acetic anhydride (250), and sodium isovalerate (75), heated for seven hours at 150°, gave no hydrocarbon, but 6 grams of  $\beta$ -2-furylacrylic acid, m. p. 140°.

Anisaldehyde (50), isovaleric anhydride (175), and sodium isovalerate (150), heated for eight hours at 150°, gave  $\alpha$ -p-methoxyphenyl- $\gamma$ -methyl- $\Delta$ -butene (22) (Moureu and Chauvet, A., 1897, i, 404) and p-methoxy- $\alpha$ -isopropylcinnamic acid,  
 $\text{OMe:C}_6\text{H}_4\text{:CH:CHPr}^\beta\text{:CO}_2\text{H}$ ,  
 needles, m. p. 134–135°.

No definite results were obtained with o-nitrobenzaldehyde, salicylaldehyde, cinnamaldehyde, or isobutaldehyde. The aliphatic aldehyde gave no hydrocarbon or acid, whilst the others reacted very sluggishly.

J. C. W.

### The Double Acid from Normal and *allo*-Cinnamic Acids.

A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, 20, 1230–1233).—The double acid can be prepared (1) by crystallisation from a solution saturated with respect to both acids, and (2) by exposing a dilute solution of sodium cinnamate (about 1%) to light for several months, evaporating to dryness, acidifying the residue with hydrochloric acid, and extracting the organic acids with hot light petroleum; the cold extract ultimately yields crystals of the double acid. A saturated solution of the two acids is in equilibrium with the *allo*-acid of m. p. 42°, inoculated with the *allo*-acid of m. p. 58° or 68°, soon crystallises, and solutions are obtained which are in equilibrium with these two modifications. If these solutions are allowed to evaporate, the double acid separates, together with the modification of the *allo*-acid used for inoculation. The double acids obtained from these solutions consist of 50% of normal acid and 50% of *allo*-acid, all melt in the same way, sintering at about 56° and being completely molten

at about 90°, and are all proved to be identical in the following way. An aqueous solution saturated with the normal acid and the *allo*-acid at the ordinary temperature, and in equilibrium with the *allo*-acid of m. p. 42°, was prepared, and to portions of this solution crystals of the double acids were added. They produced no effect whatever. Had the various double acids been different, that produced in the presence of *allo*-acid of m. p. 58° (or 68°) should have brought about crystallisation of the *allo*-acid of m. p. 58° (or 68°) and of the corresponding double acid.

The identity of the various double acids supports Büllmann's view that the three modifications of *allo*-cinnamic acid are trimorphous, and is opposed to Stobbe and Schönburg's theory that they are three different chemical individuals.

C. S.

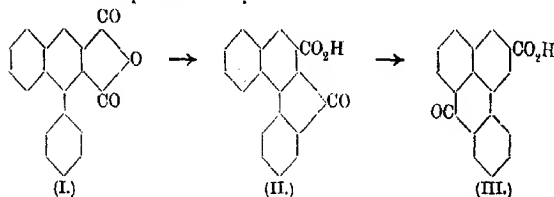
**$\alpha$ -Naphthoic sulphinide.** KURT KALCHER (*Annalen*, 1917, **414**, 244—249).— $\alpha$ -Cyanonaphthalene- $\beta$ -sulphonyl chloride, m. p. 143—144° (Friedländer and Woroschzow, A., 1912, i, 293, give 141—142°), is converted by ammonia gas in hot, dry benzene solution into  $\alpha$ -cyanonaphthalene- $\beta$ -sulphonamide, monoclinic crystals, decomp. 300—340°, which is converted by boiling *N*/10-sodium hydroxide (1½ mols.) and subsequent acidification into  $\alpha$ -naphthoic sulphinide,  $C_{10}H_6 \begin{smallmatrix} \diagup CO \\ SO_2 \diagdown \end{smallmatrix} NH$ , clusters of small prisms, m. p. 244°, together with the sodium salt of an acidic by-product. The sulphinide, which is best purified through its sodium salt, long, flattened needles, has a bitter taste and forms a methyl derivative, leaflets, m. p. 220—221°, which yields methylamine by hydrolysis with 35% hydrochloric acid at 150°. The nature of the acidic by-product has not been established.

C. S.

**A New Benzanthrone Synthesis. II. Transformation of 1-Phenylnaphthalene-2:3-dicarboxylic Anhydride into Benzanthronecarboxylic Acid.** ALFRED SCHAAERSCHMIDT and ERNST KORTEN (*Ber.*, 1918, **51**, 1074—1082. Compare A., 1917, i, 274).—1-Phenylnaphthalene-2:3-dicarboxylic anhydride (I) was first converted into 3:4-benzofluorenone-1-carboxylic acid (II) by prolonged treatment with concentrated sulphuric acid at the ordinary temperature (Stobbe, A., 1907, i, 766), and recently by means of aluminium chloride in benzene (A., 1916, i, 47). In order to hasten the older process, the authors have tried the effect of heating the anhydride with 91% sulphuric acid at 155°, the mixture being stirred for three hours. Under these conditions, two different products are obtained, namely, benzanthronecarboxylic acid, III (*loc. cit.*), which is insoluble in boiling water, and a soluble, red *sulphonic acid*,  $C_{18}H_{10}O_6S$ . This has the structure of a fluorenone, for it yields an oxime, and since it is non-fluorescent in sulphuric acid, it is most probably a derivative of 3:4-benzofluorenone-1-carboxylic acid. The same products are obtained by\*



treating this acid in the above manner, and the chief reaction can therefore be represented thus:



It illustrates the rupture of a weak five-membered ring and the establishment of a six-membered system. A similar change is suffered by 3:4-benzofluorenone itself when heated with sulphuric acid, for fluorescence is developed, but in this case the chief effect is sulphonation.

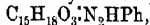
The imide of the original acid exhibits the same phenomenon most readily. 1-Phenylnaphthalene-2:3-dicarbimide, m. p. 249°, is obtained by heating the anhydride with ammonia at 240—250°. When warmed with 96% sulphuric acid at 75° for five minutes, this yields 3:4-benzofluorenone-1-carboxylic acid and its orange-red amide, m. p. 281—282°, whilst at 130°, benzanthronecarboxamide, m. p. 306°, is formed. This has been prepared from the acid (III) for comparison, and it exhibits a brilliant yellowish-green fluorescence in sulphuric acid.

J. C. W.

**A New Benzanthrone Synthesis. III.** ALFRED SCHAAER-SCHMIDT and E. GEORGEACOPOL (*Ber.*, 1918, **51**, 1082—1087. Compare A., 1917, i, 274).—As already suggested, experiments prove that when 3:4-benzofluorenone is fused with potassium hydroxide, it yields the salts of 1-phenylnaphthalene-2-carboxylic acid and *o*-naphthylbenzoic acid. The free acids may be separated by means of methyl alcohol, from which the latter acid, being only moderately soluble, crystallises in colourless rhombohedra, m. p. 161.5°. If the acids are treated with phosphorus pentachloride and then aluminium chloride, the former yields 3:4-benzofluorenone again, whilst the latter gives benzanthrone. This ketone may also be prepared by the distillation of the ammonium salt of its carboxylic acid.

J. C. W.

**Oxidation of Santonin by means of Organic Per-acids.** GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 117—121; *Gazzetta*, 1918, **48**, i, 248—253).—Oxidation of santonin by means of perbenzoic or peracetic acid results in the formation of two products: (1) *iso*-Artemisin or  $\delta$ -oxysantonin. (2) *e*-Oxysantonin,  $C_{15}H_{18}O_4$ , which crystallises in bundles of acicular prisms, m. p. 154°, at which temperature it is stable; it does not react with phenylcarbimide, and yields only a *monophenylhydrazone*,

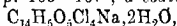


m. p. about 280°. *e*-Oxysantonin is not altered by aqueous alkali

hydroxide, but the lactone ring of its molecule may be opened by means of hot alcoholic sodium ethoxide, which changes the colour to blood-red with a transitory green fluorescence; the acid,  $C_{15}H_{20}O_5$ , thus obtained forms crystals, m. p. about  $100^\circ$ , and when heated with dilute sulphuric acid gives the original oxysantonin.

Treatment of  $\epsilon$ -oxysantonin with concentrated hydrochloric acid in the cold yields a new *chlorosantonin*,  $C_{15}H_{17}O_5Cl$ , which forms crystals, m. p. about  $196^\circ$ , and is transformed into  $\epsilon$ -oxysantonin by either cold alcoholic potassium hydroxide or boiling aqueous alcohol; by zinc dust and a few drops of acetic acid in alcoholic solution, it is converted into santonin. T. II. P.

**o-2':4'-Dihydroxybenzoyltetrachlorobenzoic Acid and 2:3:4-Trichloro-6-hydroxyxanthone-1-carboxylic Acid and some of their Derivatives.** W. R. ORNDORFF and W. A. ADAMSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1235—1256).—After surveying the results of the numerous investigations on *o*-dihydroxybenzoylbenzoic acid (Baeyer's monoresorcinphthalein, *Annalen*, 1876, **183**, 23), the authors describe in detail the preparation of *o*-2':4'-dihydroxybenzoyltetrachlorobenzoic acid from resorcinol and tetrachlorophthalic acid or its anhydride. Tetrachlorofluorescein is always formed, and some unchanged tetrachlorophthalic acid always remains, whatever the experimental conditions. The best results are obtained by heating resorcinol (4 parts) and tetrachlorophthalic acid (5 parts) for twelve to fifteen hours at a temperature not exceeding  $131^\circ$  (vapour of boiling xylene), whereby *o*-2':4'-dihydroxybenzoyltetrachlorobenzoic acid is obtained in a yield of about 90%. The substance, after purification through its acetate, forms colourless crystals containing  $2H_2O$ , and has m. p.  $227^\circ$ , with decomposition into tetrachlorofluorescein and tetrachlorophthalic anhydride. It forms a *triacetate*,  $C_{14}H_3O_5Cl_4Ac_3$ , colourless crystals, m. p.  $166$ — $167^\circ$ , a *sodium salt*,

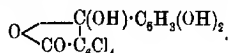


slightly grey crystals, m. p. about  $295^\circ$  (decomp.), *hydroxylammonium salt*,  $C_{14}H_5O_5Cl_4NH_2OH$ , pale yellow crystals, m. p.  $254^\circ$  (decomp.; darkening at  $230^\circ$ ), and with dry ammonia an unstable *triammonium salt* and a stable *monoammonium salt*. By bromination in glacial acetic acid, it yields *o*-3':5'-dibromo-2':4'-dihydroxybenzoyltetrachlorobenzoic acid, yellow needles, m. p.  $211$ — $212^\circ$ , which at this temperature is converted into tetrachlorophthalic anhydride and tetrachlorococin. The dibromo-acid forms a *triacetate*, colourless crystals, m. p.  $204.5^\circ$ , and an unstable, yellow *tetra-ammonium salt*, and a stable, less highly coloured *diammonium salt*.

By treatment for several hours with 5% alcoholic potassium hydroxide and subsequent acidification, the triacetate of the unbrominated acid yields 2:3:4-trichloro-6-hydroxyxanthone-1-carboxylic acid, colourless needles containing  $2H_2O$ , m. p.  $279$ — $280^\circ$  (anhydrous). The same substance is obtained by boiling the dihydroxybenzoyltetrachlorobenzoic acid with 5% aqueous sodium hydroxide. It forms a *disodium salt*,  $C_{14}H_3O_5Cl_3Na_2$ , yellow

needles, *monoacetate*, colourless needles or prisms, decomp. 220—221°, and *ammonium salt*,  $C_{14}H_4O_5Cl_2(NH_4)$ .

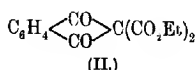
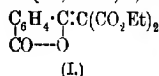
The preceding results, particularly the fact that the triacetates are stable compounds which do not undergo any change when boiled with alcohol, are interpreted by ascribing to *o*-2':4'-dihydroxybenzoyltetrachlorobenzoic acid the constitution



It seems highly probable from the results of this investigation that the formation of phthaleins takes place in two steps. First, an additive product of the phenol and the anhydride analogous to the preceding dihydroxy-acid is formed, and then this reacts with a second molecule of the phenol with the loss of water to form the phthalein. C. S.

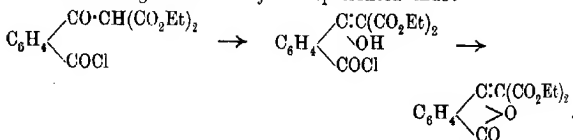
### Constitution of Phthalyl- and Succinyl-malonic Esters.

KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1918, 51, 1106—1115).—Two alternative formulæ for ethyl phthalylmalonate have been advocated, (I) by Wislicenus (*A.*, 1888, 149) and (II) by Scheiber (*A.*, 1912, i, 559):

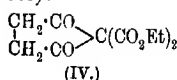
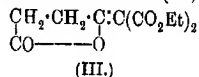


If formula II is correct, the ester should correspond in optical properties with indandiones, but this is not the case. A compound of the type I, on the other hand, should resemble ethyl benzylidene-malonate (*A.*, 1911, ii, 782), when due allowance is made for the influence of the lactone ring. It is now found that these esters are optically related, like  $\alpha$ -phenyl- $\Delta^2$ -propylene and ethylidene-phthalide,  $\text{CHPh} : \text{CHMe}$  and  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} : \text{CHMe} \\ \text{CO} \text{---} \text{O} \end{array}$ , and consequently

ethyl phthalylmalonate is correctly represented by formula I. This can be harmonised with the view that phthalyl chloride is symmetrical in structure, for the reaction with ethyl sodiomalonate can include stages which may be represented thus:



Similarly, ethyl succinylmalonate is abnormal in optical properties, and must therefore be expressed by formula III rather than by Scheiber's formula IV (*A.*, 1909, i, 363):



Ethyl phthalylmalonate (I) has m. p.  $74-75^{\circ}$ ,  $D^{25}_D$  1.1887,  $n_D$  1.53416,  $n_D$  1.54105,  $n_D$  1.56155, at  $84.4^{\circ}$ ,  $E\alpha$  2.13,  $E\beta$  2.25,  $E\gamma$  -  $\Sigma$ , 122%. 2:2-Diethylindan-1:3-dione (Freund and Fleischer, A., 1910, i. 490) has b. p.  $157-159^{\circ}/15$  mm.,  $D^{25}_D$  1.0693,  $n_D$  1.53658,  $n_D$  1.54174,  $n_D$  1.55632,  $n_D$  1.56967, at  $14.5^{\circ}$ ,  $E\alpha$  1.43,  $E\beta$  1.49,  $E\gamma$  -  $\Sigma$ , 54%,  $E\delta$  -  $\Sigma$ , 57%. 4:7-Dimethyl-2:2-diethylindan-1:3-dione (Freund and Fleischer, A., 1916, i. 317) has b. p.  $153^{\circ}/12$  mm., m. p.  $51-52^{\circ}$ ,  $D^{25}_D$  1.0174,  $n_D$  1.52107,  $n_D$  1.52598,  $n_D$  1.54051, at  $62.4^{\circ}$ ,  $E\alpha$  1.56,  $E\beta$  1.63,  $E\gamma$  -  $\Sigma$ , 63%. Ethyl succinylmalonate (III) has m. p.  $68^{\circ}$ ,  $D^{25}_D$  1.1675,  $n_D$  1.46923,  $n_D$  1.47245,  $n_D$  1.48170,  $n_D$  1.48952, at  $73^{\circ}$ ,  $E\alpha$  1.13,  $E\beta$  1.15,  $E\gamma$  -  $\Sigma$ , 41%,  $E\delta$  -  $\Sigma$ , 42%. Ethylidene-phthalide has b. p.  $152^{\circ}/11$  mm., m. p.  $64^{\circ}$ ,  $D^{25}_D$  1.1053,  $n_D$  1.56394,  $n_D$  1.57054, at  $99.4$ ,  $E\alpha$  2.29,  $E\beta$  2.36, and  $\alpha$ -phenyl- $\Delta^4$ -propylene has  $E\alpha$  1.09,  $E\beta$  1.19.

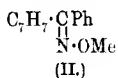
J. C. W.

**N- and O-Methyl Ethers of Ketoximes. The Four Isomeric Methyl Ethers of Phenyl *p*-Tolyl Ketoxime.** LEOPOLD SEMPER and LEO LICHTENSTADT (*Ber.*, 1918, 51, 928-942).—The *N*- and *O*-methyl ethers of ketoximes are produced in approximately equal quantities by the action of methyl sulphate on aqueous alcoholic alkaline solutions of the oximes. Thus, benzophenoneoxime yields the *N*-methyl ether, long needles, m. p.  $102-103^{\circ}$ , *hydrochloride*, m. p.  $140-143^{\circ}$ , and *O*-methyl ether, stout crystals, m. p.  $60-61^{\circ}$ . These are separated as follows: the initial product, after extraction with ether in the usual way, is triturated with light petroleum, b. p.  $30-50^{\circ}$ , which leaves most of the *N*-ether, this being recrystallised from a petroleum of b. p.  $60-70^{\circ}$ ; the solution is treated with hydrogen chloride gas, which precipitates the remaining *N*-ether as hydrochloride, and then the *O*-ether is recovered by evaporation and crystallised from alcohol. The *N*-ether exhibits a tendency to form crystalline additive compounds, of which the following are some examples: with benzophenoneoxime, 1:1, cubes, m. p.  $108-109^{\circ}$  (compare Alessandri, A., 1915, i. 412); a *demi-hydrate*, transparent leaflets, m. p.  $78-80^{\circ}$ ; a *compound* with quinol, 2:1, m. p.  $186-186.5^{\circ}$ ; a *compound* with phenylcarbimide, 1:1, m. p.  $141-142^{\circ}$ . These are highly dissociated in solution. The *O*-ether forms no such compounds.

These preliminary experiments with a simple ketoxime paved the way for an attempt to isolate the two stereoisomeric pairs of ethers from an unsymmetrical ketoxime. For the purpose of investigation, phenyl *p*-tolyl ketone was chosen. A better method for isolating the  $\alpha$ - and  $\beta$ -oximes of this has been devised (compare Hantzsch, A., 1890, 1273), and each isomeride converted into its *N*- and *O*-methyl ethers, making, therefore, the four possible isomerides.

The crude phenyl *p*-tolyl ketoxime is resolved into the two isomerides by crystallisation from 90% alcohol, which deposits most of the  $\alpha$ -oxime on cooling, the  $\beta$ -oxime being recovered by adding to the hot mother liquor about three-fifths of its bulk of hot water, and cooling. The oximes are further purified by crystallisation

from pure alcohol. The  $\alpha$ -oxime forms long, slender needles, m. p. 153—154°; the  $\beta$ -oxime crystallises in stout, transparent prisms, m. p. 136·5—137·5°. These are methylated as above, and the crude products treated in the same way. The two *N*-ethers have such tendencies to form additive compounds, however, that the products which are found to be sparingly soluble in the volatile petroleum are not the free ethers, but compounds with the unmethylated oximes. These are decomposed by dissolving them in dilute aqueous-alcoholic sodium hydroxide, precipitating the oxime by means of dilute sulphuric acid, and extracting the ethers after neutralisation of the filtrate. The  $\alpha$ -*N*-methyl ether (I) forms colourless tablets, m. p. 91—92°, and yields the following *additive compounds*: with 0·5H<sub>2</sub>O, transparent, rhombic tablets, m. p. 66—67·5°; with  $\alpha$ -phenyl *p*-tolyl ketoxime, needles, m. p. 106—107°; with the  $\beta$ -oxime, short prisms, m. p. 90—92°. The  $\alpha$ -O-methyl ether (II) crystallises in needles, m. p. 64—68°.



The  $\beta$ -*N*-methyl ether (III) forms long, glistening prisms, m. p. 113—114°, and yields *additive compounds* with the  $\beta$ -oxime (stout prisms, m. p. 81—82°) and  $\alpha$ -oxime (small cubes, m. p. 124—125°). The  $\beta$ -O-methyl ether (IV) has b. p. 184—185°/16 mm., 135—136°/0·5 mm. The two *N*-ethers are hydrolysed by boiling hydrochloric acid to phenyl *p*-tolyl ketone and  $\beta$ -methylhydroxylamine hydrochloride, and reduced by zinc dust and acetic acid to a base which may be isolated as a *hydrochloride*, C<sub>15</sub>H<sub>16</sub>NCl, m. p. 199—201°.

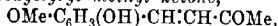
J. C. W.

### Synthesis of some Phenolic Ketones. Taste of the Ketones.

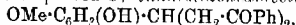
HIROSHI NOMURA and FUSATOSHI NOZAWA (*Sci. Rep. Tohoku Imp. Univ.*, 1918, 7, 79—92).—Vanillin and piperonal possess pleasant odours, whereas zingerone (methyl 4-hydroxy-3-methoxyphenylethyl ketone) and the analogous 3:4-methylenedioxyphenylethyl methyl ketone have a pungent taste, but the intermediate products in the synthesis of these substances from vanillin and piperonal, namely, 4-hydroxy-3-methoxystyryl methyl ketone and 3:4-methylenedioxy-3-methoxystyryl methyl ketone, are almost tasteless when first brought into contact with the tongue, although they gradually develop pungency. A number of compounds of similar constitution have now been examined with a view to discover the influence of constitutional variations on the taste. As in the above case of 4-hydroxy-3-methoxystyryl methyl ketone, the primary condensation product is generally less readily soluble than its final reduction product in organic solvents, and does not immediately taste pungent, whereas the reduction products are markedly pungent; styryl methyl ketone is exceptional in being readily soluble and having a very tingling taste. The presence of a free phenolic group is not essential to pungency, because phenylethyl methyl ketone, *p*-methoxyphenyl-

ethyl methyl ketone, and 3:4-methylenedioxyphenylethyl methyl ketone are all pungent. The degree of pungency, however, is greatly influenced by the position of the free hydroxyl group with respect to the ketonic side-chain; *o*-hydroxyphenylethyl methyl ketone in taste resembles 2-hydroxy-3-methoxyphenylethyl methyl ketone, and *p*-hydroxyphenylethyl methyl ketone resembles zingerone. As in these cases the hydroxyphenylethyl methyl ketones are less pungent than the corresponding hydroxymethoxyphenylethyl methyl ketones, the *m*-methoxyl group appears to increase the pungency. The influence of the simple hydrocarbon radicle attached to the ketonic group is not much greater than that of the position of the hydroxyl group, because phenyl 4-hydroxy-3-methoxyphenylethyl ketone has a pungent taste similar to zingerone.

Most of the compounds examined have been described earlier. *m*-Hydroxyphenylethyl methyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ , m. p. 85–86°, was prepared through *m*-hydroxystyryl methyl ketone, needles, m. p. 97–98°, b. p. 208–209°/14 mm., from *m*-hydroxybenzaldehyde and acetone, the condensation of these substances being effected in a 10% solution of sodium hydroxide. *p*-Hydroxyphenylethyl methyl ketone, needles, m. p. 82–83°, was obtained by the catalytic reduction of *p*-hydroxystyryl methyl ketone in ethereal solution. The condensation of 2-hydroxy-3-methoxybenzaldehyde and acetone in alkaline solution yields 2-hydroxy-3-methoxystyryl methyl ketone,



yellow crystals with  $1\text{H}_2\text{O}$ , m. p. 81–82°, or m. p. 77–77.5° if anhydrous, the catalytic reduction of which produces 2-hydroxy-3-methoxyphenylethyl methyl ketone, b. p. 206–207°/35 mm.; the pungent taste of this substance is accompanied by a paralysing effect, which is also observed with *o*-hydroxyphenylethyl methyl ketone. Vanillin and acetophenone undergo condensation in alkaline solution with the formation of phenyl 4-hydroxy-3-methoxystyryl ketone,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$ , yellow crystals, m. p. 92–93°, accompanied by vanillulidenediacetophenone,



colourless crystals, m. p. 131–132° (benzoyl derivative, colourless, m. p. 133°); on reduction in the usual way, phenyl 4-hydroxy-3-methoxystyryl ketone gave phenyl 4-hydroxy-3-methoxyphenylethyl ketone,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COPh}$ , colourless scales, m. p. 97.5–98°.

D. F. T.

**Terpenes and Ethereal Oils. CXXII. Behaviour of the Nitrosochloride Additive Compounds towards Reagents which eliminate Hydrogen Chloride.** O. WALLACH (*Annalen*, 1918, 414, 257–270).—Sodium alkyl oxides, anhydrous sodium acetate in glacial acetic acid, and dimethylaniline have been used to eliminate the elements of hydrogen chloride from nitrosochlorides, but each reagent has its disadvantages. The author now finds that an excellent conversion of a nitrosochloride into an oxime



1916, i, 213) unsaturated hydroaromatic tertiary alcohols have been converted into benzene hydrocarbons through the dibromo-additive compounds, but cases analogous to the smooth conversion of the 6-ring dibromopulegone into the 5-ring pulegenic acid under the action of alkali have hitherto not been known. The author has therefore examined the behaviour of a number of dibromo-derivatives of menthone and of carvomenthone when digested with 2% aqueous potassium hydroxide at the ordinary temperature for two to three days, and finds that the course of the reaction is determined essentially by the positions of the bromine atoms. The results may be generalised as follows: (1) Phenols are formed from dibromo-derivatives which have been obtained by the addition of bromine at an ethylenic linking adjacent to the carbonyl group and not separated from it by a substituent; for example, 1:2-dibromomenthone and 3:4-dibromocarvomenthone. The formation of the phenol does not always take place smoothly, comparatively stable monobromides sometimes being formed. (2) When the ethylenic linking is adjacent to the carbonyl group, but is separated from it by a substituent, the dibromo-derivative, for example, 4:5-dibromomenthone and 1:6-dibromocarvomenthone, readily undergoes fission of the ring with the production of an aliphatic ketonic acid with the same number of carbon atoms. (3) When the two bromine atoms are divided between the nucleus and the side-chains, or are both in the side-chains, the course of the reaction may be very varied and a general rule cannot be formulated. (4) Dibromo-derivatives in which the bromine atoms are attached to nuclear carbon atoms on either side of the carbonyl group, for example, 2:4-dibromomenthone and 1:3-dibromocarvomenthone, are converted into pentacyclic hydroxycarboxylic acids (see following abstract).

[With H. E. WOODMAN.]—When shaken for three days with 2% aqueous potassium hydroxide, 8:9-dibromomenthan-2-one, prepared by the bromination of optically active dihydrocarvone, is converted, apart from small quantities of carvacrol and carvenone, into a heavy oil, which loses hydrogen bromide and yields carvacrol when distilled in a vacuum, and is reduced to dihydrocarvone by zinc and aqueous sodium hydroxide, and is therefore probably the monobromide,  $\text{CHBr}:\text{CMe} \cdot \text{CH} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CO} \end{smallmatrix} > \text{CHMe}$ .

The crystalline dihydrocarvone dibromide, m. p. 69–70°, obtained by brominating *l*-dihydrocarvone in glacial acetic acid containing hydrogen bromide, is converted by 2% aqueous potassium hydroxide into an unsaturated *hydroxy-ketone*,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , b. p. 140°/16 mm.,  $D^{20}_D$  1.0285,  $n_D$  1.4917 (*semicarbazone*, m. p. 123–124°), which yields carvacrol by warming with dilute sulphuric acid, and is possibly 8-hydroxy- $\Delta^8$ -menthen-2-one or 8-hydroxy- $\Delta^8$ -menthen-2-one.

3:4-Dibromocarvomenthone is converted by 2% aqueous potassium hydroxide into carvacrol, and, similarly, 1:2-dibromomenthone into *m*-cresol.



[With H. E. WOODMAN and W. JESSEN.]—1:6-Dibromocarvomenthone is converted by shaking with 2% aqueous potassium hydroxide for two to three hours at the ordinary temperature, and then for one to two hours at 100° into *ε*-keto-*β*-isopropylheptonic acid, which is identified as the optically active modification by the formation of the semicarbazone, m. p. 158—159°, and the oxime, m. p. 60—63° (rising to 87—89° by recrystallisation).

[With ADOLF HALLSTEIN.]—When 1:2-dibromomenthone is shaken for sixteen to twenty hours with the quantity of 2% aqueous potassium hydroxide calculated to remove all the bromine, a *monobromide*,  $C_{10}H_{15}OBr$ , m. p. 42—43°, is obtained, together with some thymol. The monobromide is converted into thymol by heating it alone, when hydrogen bromide is evolved, or with sodium methoxide. This behaviour and the method of preparation indicate that the monobromide is 2-bromo- $\Delta^6$ -menthen-3-one or 2-bromo- $\Delta^1$ -menthen-3-one, but the substance does not react readily with bromine, and yields by oxidation with alkaline potassium permanganate oxalic acid, volatile fatty acids, and a *ketonic acid*,  $C_{10}H_{14}O_3$ , m. p. 105—106° (*silver salt*,  $C_{10}H_{13}O_3Ag$ ; *semicarbazone*, m. p. 225°); the formation of the last acid is not explicable by either of the formulæ given above.

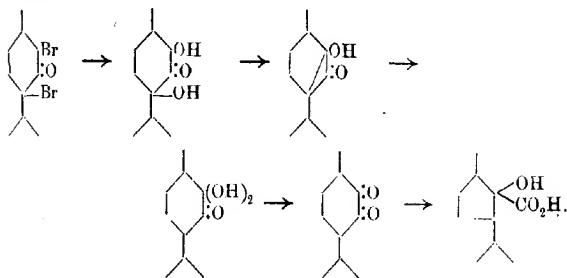
[With EMMA GROTE.]—4:5-Dibromomenthone is converted by 2% potassium hydroxide into an aliphatic *ketonic acid*,  $C_{10}H_{16}O_3$  (*silver salt*,  $C_{10}H_{17}O_3Ag$ ; *semicarbazone*, m. p. 161—163° [slowly heated] or 164—166° [rapidly heated]), which is probably *ε*-keto-*β*-dimethylheptonic acid,  $COPr^{\delta}-CH_2-CH_2-CHMe-CH_2-CO_2H$ .

An unsatisfactory attempt to prepare  $\Delta^{4(5)}$ -menthen-3-one from 4-bromomenthan-3-one is described. C. S.

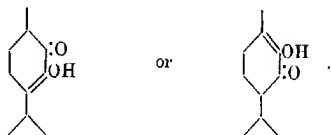
**Terpenes and Ethereal Oils. CXXIV. Method of Transforming Hexacyclic Ketones into *cyclo*Pentanones Based on the Conversion of Dibrominated *cyclo*Hexanones into Pentacyclic  $\alpha$ -Hydroxy-carboxylic Acids.** O. WALLACH [with MATHILDE GERHARDT and WILHELM JESSEN] (*Annalen*, 1918, **414**, 296—366).—A portion of the work has already appeared (*A.*, 1916, i, 437).

The dibrominated *cyclo*hexanones which contain the bromine atoms in such positions that pentacyclic  $\alpha$ -hydroxy-carboxylic acids are produced by the action of alkalis (see preceding abstract) are in general easily obtained by treating the *cyclo*hexanone in glacial acetic acid solution with four atoms of bromine. Since *cyclo*pentanones are known only in small number, whilst *cyclo*hexanones can be obtained in large numbers, not only from natural sources, but also from phenols by Sabatier's method and by Knoevenagel's synthesis, it is of importance to find out whether it is possible quite generally to convert *cyclo*hexanones into pentacyclic  $\alpha$ -hydroxy-carboxylic acids with the same number of carbon atoms, from which *cyclo*pentanones can be obtained by oxidation. Up to the present time, nine *cyclo*hexanones have been converted into *cyclo*pentanones by the elimination of a nuclear methylene group, the penta-

cyclic  $\alpha$ -hydroxy-carboxylic acids being intermediate products. The formation of these would be easily explicable if the original dibromocyclohexanone contained a  $\text{CBr}_2$  group adjacent to the carbonyl group, because the alkali would then produce an ortho-diketone, from which the pentacyclic  $\alpha$ -hydroxy-carboxylic acid would be formed by a benzilic acid transformation. This simple explanation is inapplicable, for two reasons: (1) It is proved quite definitely that by direct substitution in menthone and carvomenthone, the two bromine atoms are not attached to one and the same carbon atom, but that one bromine atom replaces the tertiary hydrogen atom adjacent to the carbonyl group and the other enters the methylene group on the other side of the carbonyl group. (2) Although compounds having the composition of  $\alpha$ -diketones can be isolated, they do not exhibit the properties of such substances, but behave as unsaturated ketols. Such compounds derived from the dibromomenthone and the dibromocarvomenthone are identical and yield the same pentacyclic hydroxy-carboxylic acid. The author's explanation is represented schematically: for dibromomenthone,



and similarly for the dibromocarvomenthone; the same  $\alpha$ -diketone is formed in both cases, but when isolated isomerises to the unsaturated ketol,



The bromination of 1:3-dimethylcyclohexan-5-one in cold glacial acetic acid produces two dibromo-compounds, an  $\alpha$ -dibromide,  $\text{C}_8\text{H}_{12}\text{OBr}_2$ , needles, m. p.  $163\text{--}164^\circ$  (decomp.), which is scarcely attacked by alkali, and an isomeric  $\beta$ -dibromide, prisms, m. p.  $60\text{--}61^\circ$ , which is converted by 2% aqueous potassium hydroxide into the ketol,  $\text{C}_8\text{H}_{12}\text{O}_3$ , m. p.  $71\text{--}72^\circ$ . The ketol, which is removed from the acidified liquid by steam, is converted by con-

centrated aqueous potassium hydroxide at  $140^{\circ}$  into 4-hydroxy-1:3-dimethylcyclopentane-4-carboxylic acid,  $C_8H_{14}O_3$ , colourless crystals, m. p.  $92-93^{\circ}$ , which yields 1:3-dimethylcyclopentane-4-one, b. p.  $152-154^{\circ}$ ,  $D_{17}^{20} 0.8950$ ,  $n_D^{20} 1.4330$  (semicarbazone, m. p.  $165-166^{\circ}$ ), by warming with lead peroxide and sulphuric acid. C. S.

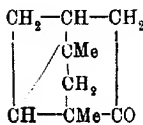
**Terpenes and Ethereal Oils. CXXV. Compounds of the Eucarvone Series.** O. WALLACH [with MAX STANDACHER], (*Annalen*, 1918, **414**, 367-375).—Assuming the constitution given to  $\beta$ -dihydroeucarvoxime (*Annalen*, 1914, **403**, 87) to be correct, the reduction of the substance should yield tetrahydroeucarvylamine. This is found to be so. When reduced by sodium and alcohol, the oxime is converted into a base,  $C_{10}H_{16} \cdot NH_2$ , b. p.  $208.5^{\circ}$ ,  $D_{21}^{20} 0.8680$ ,  $n_D^{20} 1.4665$ , which forms a carbamide, m. p.  $139^{\circ}$ , phenyl carbamide, m. p.  $143-146^{\circ}$ , trimethylammonium iodide, m. p. about  $200^{\circ}$ , and an acetyl derivative, m. p.  $110.5^{\circ}$ , the last being identical with the substance obtained by acetylating the base prepared by the reduction of tetrahydroeucarvoxime.

By bromination in glacial acetic acid at  $0^{\circ}$ , tetrahydroeucarvone yields a monobromo-derivative,  $C_{10}H_{17}OBr$ , crystals, m. p.  $32^{\circ}$ , which is converted by 3% aqueous potassium hydroxide into hydroxytetrahydroeucarvone,  $OH \cdot C_{10}H_{17}O$ , b. p.  $98^{\circ}/12.5$  mm.,  $D_{20}^{20} 0.9810$ ,  $n_D^{20} 1.4626$  (semicarbazone, m. p.  $193^{\circ}$ ; oxime, m. p.  $84^{\circ}$ , which forms a crystalline sodium salt). The hydroxy-compound is reduced to a glycol,  $C_{10}H_{18}(OH)_2$ , b. p.  $112-117^{\circ}/4$  mm., by sodium and alcohol, and yields a chromate,  $(C_{10}H_{17}O)_2CrO_3$ , when treated with sulphuric acid and chromium trioxide dissolved in a little water, at a temperature not exceeding  $0^{\circ}$ .

When treated with bromine (2 mols.) in glacial acetic acid without cooling, tetrahydroeucarvone yields dibromotetrahydroeucarvone,  $C_{10}H_{16}OBr_2$ , colourless prisms, m. p.  $68^{\circ}$ , which is converted by 4% aqueous potassium hydroxide at  $100^{\circ}$  into an acid,  $C_{10}H_{16}O_2$ , crystals, m. p.  $91.5-92.5^{\circ}$  (silver salt,  $C_{10}H_{15}O_2Ag$ ). The acid is saturated, odourless, and somewhat easily volatile with steam; its constitution has not yet been determined. When treated with methyl-alcoholic sodium methoxide, dibromotetrahydroeucarvone yields a substance,  $C_{10}H_{16}O_2$ , b. p.  $218-219^{\circ}$ ,  $D_{20}^{20} 0.979$ ,  $n_D^{20} 1.4698$ , isomeric with the preceding acid, the nature of which has not yet been ascertained. C. S.

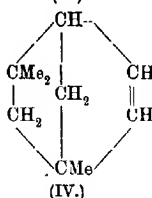
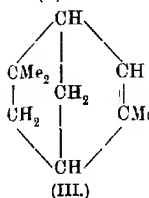
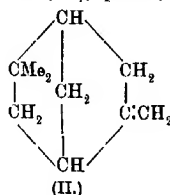
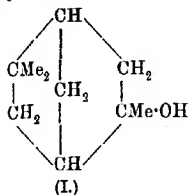
**Isomerisation Product of Carvone in the Light. Carvone camphor. II.** E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 238-242. Compare A., 1915, i, 425).

—When the oxime of carvonecamphor is heated with 20% sulphuric acid on the water-bath, isocarvonecamphor is obtained, the yield being almost theoretical. Phosphorus pentachloride reacts with the oxime in chloroform solution, giving 2-chlorocymene. From these and other reactions previously described, the annexed constitution is suggested for carvonecamphor.



R. V. S.

**The Partial Synthesis of  $\beta$ - and  $\gamma$ -Fenchene.** GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. Fennicae*, 1917, A, [x], 15, 1—15; from *Chem. Zentr.*, 1918, i, 622. Compare A., 1917, i, 398, 466).—In extension of the earlier conversion of *dl*- $\alpha$ -fenchocamphorone into  $\alpha$ -fenchene, the authors have treated *dl*- $\beta$ -fenchocamphorone with magnesium methyl iodide, with production of *methyl- $\beta$ -fenchocamphorol* (annexed formula, I), prisms, m. p.



36—67°, b. p. 77°/9 mm., 85°/15 mm.; *phenylurethane* derivative,  $C_{17}H_{25}O_2N$ , obtained by the action of phenylcarbimide, needles, m. p. 133·5—134°; *acetyl* derivative,  $C_{12}H_{20}O_2$ , b. p. 212·5°/766 mm., 90·5—81°/8 mm.,  $D_4^{20}$  0·9769,  $n_D^{20}$  1·45884. When heated with potassium hydrogen sulphate, *methyl- $\beta$ -fenchocamphorol* yields a mixture of hydrocarbons consisting mainly of *dl*- $\beta$ -fenchene (formula II), b. p. 151—153°,  $D_4^{20}$  0·8596,  $n_D^{20}$  1·46581, with an endocyclic  $\gamma$ -fenchene (formula III), b. p. 146—148°,  $D_4^{20}$  0·8539,  $n_D^{20}$  1·46063, identical with the product of the interaction of *dl*-fenchyl alcohol and potassium hydrogen sulphate; *dl*- $\beta$ -fenchene on oxidation with potassium permanganate gives *dl*-hydroxy- $\beta$ -fenchenic acid, needles, m. p. 124—125° (*acetyl* derivative,  $C_{13}H_{18}O_4$ , scales, m. p. 117—118°); the acid is oxidised by lead dioxide and sulphuric acid to *dl*- $\beta$ -fenchocamphorone, and this further by potassium permanganate to *apofenchocamphoric* acid. The endocyclic fenchene (formula IV) described earlier (Roschier, *Dis.*, Helsinki, 1917), and termed *isallofenchene* by Semmler and *sofenchylene* by Qvist, should be designated  $\delta$ - or *iso*-fenchene. The compound now described by the authors as  $\beta$ -fenchene has been earlier termed *isofenchene* by Semmler and *Dd*- (or *Ll*-) fenchene by Wallach.

D. F. T.

**Terpenes and Ethereal Oils. CXX.** O. WALLACH (*Annalen*, 1917, 414, 195—233).—Most of the work has been already published (A., 1916, i, 213). The following is new.

[With KURT PELIKAN.]—From the accepted formulæ of pinol hydrate and dihydrocarveol, the expectation is justifiable that the reduction product of the former will be identical with the menthane-2:8-diol obtained from the latter by the addition of water (Wallach, *Annalen*, 1911, **380**, 161). The expectation, however, is not fulfilled. *i*-Pinol hydrate yields by reduction a glycol, dihydropinol hydrate, m. p. 139—141°, whilst the *i*-glycol obtained from dihydrocarveol has m. p. 108—109°. Also, *d*-pinol hydrate (sobrerol) reduced in methyl-alcoholic solution by Paal's method yields a glycol,  $C_{10}H_{18}(OH)_2$ , m. p. 158—159°,  $[\alpha]_D^{20} -40.26'$  in alcohol, whilst the glycol derived from the optically active dihydrocarveol has m. p. 113—114°.

The behaviour of pinol hydrate on reduction, therefore, has been examined. When it is reduced by hydrogen and colloidal palladium in the absence of free acid, there occurs, in addition to the normal reduction, a by-reaction in which the pinol hydrate is dehydrated and the resulting unsaturated monohydric alcohol is reduced to tetrahydrocarveol. This result not only again shows that unsaturated glycols are not always smoothly reduced to the saturated glycols in the presence of colloidal metal (compare A. 1912, i, 878), but is also a further proof that in pinol hydrate a hydroxyl group occurs in position 2.

*i*- or *l*-Dihydropinol hydrate is converted into terpinene dihydrobromide by treatment with hydrogen bromide in glacial acetic acid. A similar transformation is not produced by hydrogen chloride. Moreover, the menthane-2:8-diol obtained from dihydrocarveol does not behave in this way.

It is shown that dihydropinol hydrate is not identical with menthane-1:4-diol or with *menthane-2:4-diol*, obtained by reducing sabinene glycol by Paal's method. The latter diol has b. p. 135—140°/9 mm.; the distillate solidifies completely (m. p. 93—94°), but separates as an oil from solvents on account of its great solubility. When dehydrated by oxalic acid and water, it yields a small quantity of a hydrocarbon, b. p. 172—182°,  $D_D^{20}$  0.866, showing the reactions of terminene, the main product being an unsaturated alcohol,  $C_{10}H_{17}OH$ , b. p. 219—221°,  $D_D^{20}$  0.9250,  $n_D^{20}$  1.4790, which yields carvenone by oxidation with chromic acid and tetrahydrocarveol by reduction by Paal's method. The alcohol would therefore appear to be  $\Delta^3$ -menthene-2-ol, but that  $\Delta^{4(8)}$ -menthene-2-ol is also present is indicated by the formation of acetone when the alcohol is oxidised by potassium permanganate. When *i*-dihydropinol hydrate is warmed with oxalic acid and water, the main product is a saturated oxide having an odour of cineole; dihydrocarveol is formed as a by-product. C. S.

**The Pungent Principles of Ginger. II.** HIROSHI NOMURA (*Sci. Rep. Tohoku Imp. Univ.*, 1918, **7**, 67—77. Compare T., 1917, 111, 769).—By distillation of the pungent principles of Japanese ginger under reduced pressure, the author has been able to isolate

in addition to zingerone, a substance, *shogaol*,  $C_{17}H_{24}O_3$ , b. p.  $175-185^\circ/0.4-0.5$  mm.,  $231-238^\circ/15.5$  mm., M.W. in benzene 262,  $D_4^{20}$  1.0448,  $n_D^{20}$  1.52467; this substance is phenolic (*acetyl* derivative, b. p.  $183-188^\circ/0.6$  mm.; *methyl* ether, b. p.  $160-165^\circ/0.06$  mm.; *ethyl* ether, b. p.  $181-186^\circ/0.65$  mm.), and also contains a methoxy-group; the third oxygen atom is probably ketonic. Oxidation of the ethyl ether with alkaline permanganate yields ethylvanillic acid, so that the constitution of shogaol may be represented  $OH \cdot C \begin{smallmatrix} \diagup C(OMe) : CH \\ \diagdown CH - CH \end{smallmatrix} \gg C \cdot C_{10}H_{17}O$ . From the facts that on reduction in ethereal solution with hydrogen and platinum-black shogaol yields *dihydrosogaol*,  $C_{17}H_{26}O_3$ , b. p.  $166-169^\circ/0.15$  mm., and that the molecular refraction of shogaol greatly exceeds the calculated value, it appears probable that shogaol is a  $\beta$ -unsaturated ketone. D. F. T.

**Some Derivatives of the Pyrrol Methyl Ketones with Furfuraldehyde.** C. FINZI and E. VECCHI (*Gazzetta*, 1917, 47, ii, 10-19).—Whereas benzaldehyde reacts equally easily with the 2- and 3-acetyl derivatives of pyrrole, the results now described show that furfuraldehyde reacts well and almost quantitatively with acetyl groups in the 2-position, but that the reaction with a 3-acetyl group appears to be influenced by the presence of some substituent group in the pyrrole nucleus. In view of their analogy to cinnamyl derivatives, the compounds obtained by the condensation of furfuraldehyde with the acetylpyrroles are termed *furacryl* derivatives.

The compound,  $\begin{smallmatrix} CH \cdot CH \\ | \\ CH \cdot NH \end{smallmatrix} \gg C \cdot CO \cdot CH : CH \cdot C_4H_3O$ , obtained by the interaction of 2-acetylpyrrole and furfuraldehyde, forms slightly iridescent, yellow needles, m. p.  $134-135^\circ$ .

The compound,  $\begin{smallmatrix} CH \cdot CMe \\ | \\ CMe \cdot NH \end{smallmatrix} \gg C \cdot CO \cdot CH : CH \cdot C_4H_3O$ , obtained from 2-acetyl-3:5-dimethylpyrrole and furfuraldehyde, forms sulphur-yellow needles, m. p.  $181-182^\circ$ .

The compound,  $C_4HNMe_3(CO_2Et) \cdot CO \cdot CH : CH \cdot C_4H_3O$ , formed from ethyl 2-acetyl-3:5-dimethylpyrrole-4-carboxylate and furfuraldehyde, crystallises in lemon-yellow, prismatic needles, m. p.  $184-185^\circ$ . The corresponding acid,

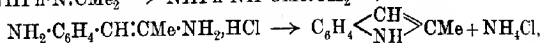
$C_4HNMe_3(CO_2H) \cdot CO \cdot CH : CH \cdot C_4H_3O$ , obtained either by hydrolysing this ester or by starting from the pyrrolecarboxylic acid, forms minute, yellow, prismatic crystals, m. p.  $287-288^\circ$ ; the insoluble silver salt was analysed.

The compound,  $\begin{smallmatrix} CO_2Et \cdot C \equiv CMe \\ | \\ NH \cdot CMe \end{smallmatrix} \gg C \cdot CO \cdot CH : CH \cdot C_4H_3O$ , obtained from ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate and furfuraldehyde, forms sulphur-yellow needles, m. p.  $149-150^\circ$ . The corresponding acid forms minute, straw-yellow, prismatic needles, m. p.  $179-180^\circ$  (decomp.); the corresponding silver salt was analysed.

The compound,  $\begin{matrix} \text{CH}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_4\text{H}_9\text{O}) \\ \text{CH}\cdot\text{C}(\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_4\text{H}_9\text{O}) \end{matrix} > \text{NH}$ , obtained from 2:5-diacetylpyrrole and furfuraldehyde, forms lemon-yellow crystals, m. p. 238—240°, and dissolves in concentrated sulphuric acid in the cold, giving an intense blue coloration with a violet border; dilution of this solution results in the precipitation of the unaltered compound. The corresponding dicinnamyl derivative is very slightly soluble in cold concentrated sulphuric acid, and only in the hot dissolves somewhat, giving a reddish-violet coloration.

The compound,  $\begin{matrix} \text{C}\text{Ac}\cdot\text{CMe} \\ \parallel \\ \text{CMe}\cdot\text{NH} \end{matrix} > \text{C}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_4\text{H}_9\text{O}$ , formed from 2:4-diacetyl-3:5-dimethylpyrrole and furfuraldehyde, crystallises in tufts of prismatic needles, m. p. 170°, and dissolves in concentrated sulphuric acid, giving a carmine coloration, changing later to amaranth; on dilution, this solution deposits the original compound. The corresponding dicinnamyl derivative dissolves only slightly and slowly in cold concentrated sulphuric acid, giving the orange-yellow coloration shown with all the furacryl and cinnamyl derivatives of the pyrroles as yet examined. T. H. P.

**New Synthesis of Tetraphenylpyrrole.** GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1918, 113, 639—645).—Adopting a hypothesis, represented by the following scheme, to account for the conversion of phenylhydrazones into indoles,  $\text{NHPh}\cdot\text{N}\cdot\text{CMe}_2 \rightarrow \text{NHPh}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}_2 \rightarrow$

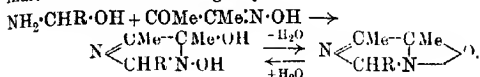


the authors record the process of reasoning which led them to expect that azines of substances containing the group  $\cdot\text{CH}_2\cdot\text{CO}$  would, under correct conditions, be transformed into pyrroles. Their expectation was fulfilled in the case of phenylbenzylketazine, which yielded tetraphenylpyrrole and ammonium chloride when heated at 180° in a current of dry hydrogen chloride. The simple aliphatic azines, such as acetaldazine and dimethylketazine, yield the corresponding pyrazoles and pyrazolines.

Ketazines are obtained in excellent yield by heating the ketone with the calculated quantity of hydrazine sulphate in boiling aqueous alcohol in the presence of an excess of sodium acetate. C. S.

**Course of the Reaction between Diacetyl [Dimethyl Diketone] Monoxime and Aldehydes in the Presence of Ammonia. Formation of Dihydroxydihydroglyoxalines.** OTTO DIELS (Ber., 1918, 51, 965—976).—The author has already shown that when dimethyl diketone monoxime is condensed with aldehydes in the presence of a concentrated alkali hydroxide, oximes of unsaturated  $\alpha\beta$ -diketones are formed, thus:  $\text{R}\cdot\text{CHO} + \text{COMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH} = \text{H}_2\text{O} + \text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}\text{Ac}\cdot\text{N}\cdot\text{OH}$  (A., 1913, i, 875), whereas compounds of the type  $\text{RC}\begin{matrix} \text{O} \\ \parallel \\ \text{N}\cdot\text{CMe} \end{matrix} > \text{O}$  are produced if

concentrated hydrochloric acid is the condensing agent (A., 1915, i, 690). It is now found that a reaction also takes place in the presence of aqueous-alcoholic ammonia, the products being characterised by the fact that they readily lose water on warming and combine with it again most easily. As ammonia takes part in the reaction, it is assumed that the aldehydes condense with the oxime in the form of their ammonia compounds, and the process is indicated in the following way:



The products are therefore dihydroxydihydroglyoxalines.

For example, benzaldehyde yields the compound,  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$ , which crystallises in compact needles, forms colourless, crystalline salts with sodium hydroxide or nitric and sulphuric acids, and melts at  $120-121^\circ$  with evolution of water, thereby changing into the compound,  $\text{C}_{11}\text{H}_{12}\text{ON}_2$ , m. p.  $180^\circ$ . On oxidation with dilute chromic acid, it yields acetic and benzoic acids and 3-phenyl-5-

methyl-1:2:4-oxadiazole,  $\text{O} \begin{array}{c} \text{N}=\text{CPh} \\ \diagup \\ \text{CMe}\cdot\text{N} \end{array}$ , which has m. p.  $41^\circ$ , b. p.

$252-253^\circ/763$  mm., and the odour of methyl salicylate, and is the "benzenylazoximethenyl" described by Tiemann and Krüger (A., 1884, 1326). On reduction with zinc dust and 50% acetic acid, it forms a base,  $\text{C}_{11}\text{H}_{14}\text{N}_2$ , which has m. p.  $242^\circ$ , sublimes readily, and gives well-defined salts with the mineral acids.

Furfuraldehyde reacts at about  $40-60^\circ$  to give the compound,  $\text{C}_9\text{H}_{12}\text{O}_3\text{N}_2$ , which crystallises from hot water in prisms, forms a crystalline hydrochloride and sulphate, dissolves in dilute alkali hydroxides, gives a pale amethyst solution in concentrated sulphuric acid which is changed to emerald-green on adding a trace of nitric acid, melts at  $112-113^\circ$ , losing water and changing into the compound,  $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$ , m. p.  $170-171^\circ$ . At  $0^\circ$ , the product is hydrofurfuramide, which does not react further with dimethyl diketone monoxime unless the mixture is warmed with a little free ammonia.

Cinnamaldehyde forms the compound,  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$ , which crystallises in glistening, pale yellow prisms, m. p.  $138-139^\circ$  (decomp.), and gives very sparingly soluble salts with the mineral acids.

Acetaldehyde-ammonia and dimethyl diketone monoxime yield the compound,  $\text{C}_{10}\text{H}_{17}\text{O}_3\text{N}_3$ , in large crystals, m. p.  $129-130^\circ$ . This seems to be loosely compounded of one molecule of the oxime and the expected compound,  $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_2$ , analogous to the above ( $\text{R}=\text{Me}$ ), which crystallises in druses, m. p.  $80-81^\circ$ , and loses water to form the compound,  $\text{C}_6\text{H}_{10}\text{ON}_2$ , m. p.  $134^\circ$ , for resolution into these two products can be effected by warming with water, alkalis, acids, or phenylhydrazine.

J. C. W.

**Nature of Cyclic Quinoneimide Dyes.** F. KEHRMANN (Annalen, 1917, 414, 131-188).—A theoretical paper containing a discussion of the results of investigations of the constitutions of



cyclic quinoneimine dyes. The classes discussed are azonium compounds (azines, safranines, indulines), azthionium (thionines), azoxonium (azoxines), carboxonium and carbothionium (pyronines, rosamines, thiopyronines, cyanopyronines, cyanoacridines), and acridonium. The discussion starts with the desmotropy of 6-hydroxynaphthaphenazine recorded by Kehrmann and Messinger in 1891, and this strikes the key-note of the author's treatment of the subject. The dyes are in general regarded as desmotropic substances which acquire the ortho- or the para-quinonoid structure according to the conditions; for example, rosinduline and induline salts are orthoquinonoid, but the free bases are paraquinonoid.

C. S.

**Constitution of Pyronine.** J. VON BRAUN (*Ber.*, 1918, 51, 440—441).—Polemical, replying to Kehrmann's references (preceding abstract) to the author's views (*A.*, 1916, i, 663).

J. C. W.

**Acylyated *p*-Phenylenemethyldiamines.** GILBERT T. MORGAN and WILLIAM ROBINSON GRIST (*T.*, 1918, 113, 688—694).—Acyly derivatives of *p*-phenylenediamine are of technical importance for the production of bisazo-dyes. The following intermediates have been prepared from methylaniline: *p*-nitromethylformanilide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CHO}$ , pale yellow prisms, m. p. 118—120°; *p*-aminomethylformanilide (as *formyl-p*-phenylenemethyldiamine), colourless needles, m. p. 132°; the corresponding *acetanilide*, colourless needles, m. p. 63°. The last two substances by treatment with nitrous anhydride in dry acetone at  $-10^\circ$  yield *formylmethylaminobenzene-4-diazohydroxide*,  $\text{CHO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OH}$ , greyish-white granules, decomp. 131—132°, and the corresponding *acetyl* compound, decomp. 131—132°, respectively, which react with dry  $\beta$ -naphthol to form *formylmethylaminobenzene-4-azo- $\beta$ -naphthol*, ill-defined crystals, m. p. 160—161°, and the corresponding *acetyl* compound, red tablets or flattened needles, m. p. 139°; the two *azo- $\beta$ -naphthols* were also obtained by coupling the diazotised *p*-aminomethylacylanilides with  $\beta$ -naphthol in alkaline solution.

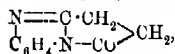
C. S.

**Preparation of 4-Diallylamino-1-phenyl-2:3-dimethyl-5-pyrazolone.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.P. 304983; from *Chem. Zentr.*, 1918, i, 789).—4-Diallylamino-1-phenyl-2:3-dimethyl-5-pyrazolone, colourless crystals, m. p. 90°, possessing antipyretic and narcotic effect, is obtainable by the action of allyl haloids on 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone in the warm, preferably in the presence of a solvent or diluent, and with the addition of some substance to remove the acid produced.

D. F. T.

**Theory of Ring Closure.** RICHARD MEYER and HERMANN LÜDERS (*Annalen*, 1918, 415, 29—50).—Since Thiele and Falk (*A.*, 1906, i, 750) have shown that Anderlini's so-called *o*-phenylene

phthalamide, prepared from *o*-phenylenediamine and phthalic acid (A., 1894, i, 315), is really 2-carboxyphenylbenziminazole, the authors have reinvestigated the action of *o*-phenylenediamine with succinic acid, and find that two compounds only are formed, not three as stated previously (A., 1903, i, 442; 1906, i, 765), the substance, m. p. 236°, supposed to be the 8-ring *o*-phenylenesuccinamide being identical with benziminazole-2-propionic acid. It yields a *methyl* ester, quadratic leaflets, m. p. 144–145°, *ethyl* ester, needles, m. p. 135–136°, and *amide*, prismatic needles, m. p. 254° (decomp.); the *silver* salt, small prisms, *copper* salt, blue plates, and *platinichloride*, yellow crystals, are described, and also the *platinichloride* of the methyl ester. By heating at 230–240°, it loses water and yields 1:2-*propionylenebenziminazole*,



colourless needles, m. p. 171°.

Since, therefore, the compounds obtained from *o*-phenylenediamine and phthalic acid and succinic acid respectively are 5-ring, not 8-ring compounds, the behaviour of the diamine with other dibasic acids (Meyer, *loc. cit.*) requires reinvestigation. Cox (*Diss.*, Strassburg, 1908) has already shown that the product from the diamine and malonic acid is easily split into its generators, does not contain a carboxyl group, and is the 7-ring *o*-phenylenemalonamide, as stated by Meyer. It is now shown that the product from *o*-phenylenediamine and ethyl *isosuccinate* behaves similarly, and is, as stated previously (*loc. cit.*), the 7-ring *o*-phenyleneisossuccinamide, although its infusibility and sparing solubility suggest that the molecule is polymerised.

The reactivity of the methine hydrogen atom in ethyl *isosuccinate* has been investigated. No reaction occurs with formaldehyde or benzaldehyde, and the sodio-derivative of the ester does not yield condensation products with succinyl chloride or phthalyl chloride, but reacts with benzoyl chloride and with cinnamoyl chloride in dry ether to form *ethyl α-benzoylisosuccinate*,  $\text{CMeBz}(\text{CO}_2\text{Et})_2$ , small, quadratic plates, m. p. 36–38°, b. p. 193–195°/18 mm., and *ethyl α-cinnamoylisosuccinate*, a pale yellow, viscous liquid, b. p. 225–230°/15 mm., respectively. *isoSuccinic* acid and benzoic or cinnamic acid are obtained when attempts are made to hydrolyse these esters, and the reaction with phenylhydrazine results in the formation of benzoyl- or cinnamoyl-phenylhydrazine and ethyl *isosuccinate*.

When heated slowly, *m*-nitrophthalanilic acid apparently has m. p. 240° (Meyer, *loc. cit.*), but when heated rapidly it melts at 202° with violent foaming (Tingle and Rolker, A., 1909, i, 28), resolidifies, and melts again at 240°. This phenomenon is due to the conversion of the anilic acid into the anil, which has m. p. 240–242°. The anilic acid crystallises in colourless needles, not faintly yellow, as previously stated (Meyer, *loc. cit.*). The fusion of *p*-nitrophthalanilic acid is similar; at 190–192° fusion occurs

with violent foaming, and the product resolidifies and melts again at 260°, the m. p. of the anil. *o*-Nitrophthalanilic acid, yellow leaflets, has m. p. 146—148° (without decomp.), but at 190—206° it loses water and yields the anil, colourless needles, m. p. 200—201°. *m*-Nitrosuccinanilic acid has m. p. 179° (stated previously, 181—182°, *loc. cit.*), and the anil has m. p. 174°.

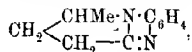
C. S.

**Action of Ortho- and of Peri-diamines, and of Ethylenediamine, on  $\gamma$ -Lactones.** A. BISTRZYCKI and WALTHER SCHMUTZ

(*Annalen*, 1918, **415**, 1—28).—The behaviour of *o*-phenylenediamine and of 1:8-naphthylenediamine with lactones derived from certain alcohol-acids has been examined; two molecules of water are eliminated and benziminazole derivatives produced. When lactones derived from phenolic acids are employed, benziminazole derivatives are again obtained, but the condensation does not proceed beyond the elimination of one molecule of water. Thus phthalide and *o*-phenylenediamine hydrochloride, heated at from about 180° to 200°, yield the hydrochloride of *o*-benzylenebenziminazole, m. p. 212—213° (Thiele and Falk, A., 1906, i, 751, give 210°) (*picrate*, yellow needles, decomp. 243·5°), whilst phthalide and 1:8-naphthylenediamine in a similar reaction yield the hydrochloride of benzyleneperimidine (phthaloperidine). Whilst phthalphenone does not react with *o*-phenylenediamine (or its hydrochloride) or with *p*-ethoxy-*o*-phenylenediamine, phenolphthalein reacts extremely vigorously with the former at 230°, yielding

*di-p-hydroxyphenylbenzylenebenziminazole*,  $\begin{matrix} \text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2\cdot\text{N}\cdot\text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4\text{---C:N} \end{matrix}$ ,

needles, decomp. 354—355°, which gives a colourless solution in dilute aqueous potassium hydroxide, and forms a *picrate*, stout prisms, m. p. 203—204°, and *diacetate*, best isolated in the form of the *picrate*,  $\text{C}_{30}\text{H}_{25}\text{O}_{11}\text{N}_5$ , yellow needles, decomp. 285·5—286°. When a mixture of valerolactone and *o*-phenylenediamine is heated finally at 270°, 1:2-(1'-methyltrimethylene)-benziminazole,



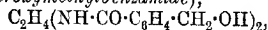
is obtained in bad yield as a brown oil; the *picrate*, yellow, microscopic prisms, has m. p. 222—224° (darkening).

*o*-Phenylenediamine and the lactone of *o*-hydroxydiphenylacetic acid react quantitatively at 120—130° to give 2-*o*-hydroxybenzhydrylbenziminazole,  $\text{C}_6\text{H}_4\begin{matrix} \text{N} \\ \text{---} \end{matrix}\text{C}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , m. p. 246—247°, which separates from ethyl alcohol or benzene in microscopic, colourless leaflets containing 1 mol. of solvent, and forms a *picrate*, stout, yellow prisms, m. p. 216°, with previous darkening; attempts to eliminate a second molecule of water by fusion with phosphoric oxide or zinc chloride were unsuccessful. The same lactone reacts with *p*-ethoxy-*o*-phenylenediamine to form

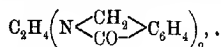
4(or 3)-ethoxy-2-o-hydroxybenzhydrylbenziminazole,

$C_{22}H_{20}O_3N_2, H_2O$ ,  
colourless prisms, m. p.  $110-120^\circ$ , with loss of the water of crystallisation, with 1:8-naphthylenediamine at  $70-100^\circ$  to form 2-o-hydroxybenzhydrylperimidine,  $C_{10}H_8 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CHPh} \cdot C_6H_4 \cdot \text{OH}$ , colourless, microscopic plates, m. p.  $295-297^\circ$  (decomp.), and with 1:2-naphthylenediamine at  $120-140^\circ$  quantitatively to form 2-o-hydroxybenzhydrylnaphthiminazole,  $C_{24}H_{18}ON_2$ , colourless, microscopic prisms, m. p.  $294-295^\circ$ , in which it has not been determined whether the NH-group is attached to the naphthalene nucleus in the  $\alpha$ - or the  $\beta$ -position. The lactone of 2-hydroxy-5-methyltriphenylacetic acid does not react with phenylenediamine or its hydrochloride.

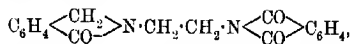
The behaviour of ethylenediamine with lactones is quite different from that of aromatic diamines. When phthalide (2 mols.) dissolved in absolute alcohol is boiled with a 50% aqueous solution of ethylenediamine (1 or 2 mols.), an additive compound, NN'-ethylenebis-(2-hydroxymethylbenzamide),



colourless needles, m. p.  $183.5^\circ$ , is obtained on cooling after pouring into water, which forms a diphenylurethane,  $C_{22}H_{30}O_4N_4$ , colourless needles, decomp.  $190^\circ$  (rapidly heated), when heated with phenylcarbimide at  $160^\circ$ , and is oxidised by chromic and glacial acetic acids to the dicarboxylic acid, which immediately changes to diphtalylethylenedi-imide by loss of water. The additive compound loses water above its m. p. and undergoes a partial change into NN'-ethylenediphtalimidine,



colourless prisms or needles, m. p.  $227.5-229^\circ$ , which is also obtained in 80-90% yield by heating phthalide (2 mols.) and ethylenediamine (1 mol.) at  $300^\circ$  for three hours. Ethylenediphtalimidine is quite stable to boiling aqueous or alcoholic potassium hydroxide. By treatment with boiling chromic and pure acetic acids, it can be oxidised successively to NN'-ethylene-phthalimidephthalimidine,

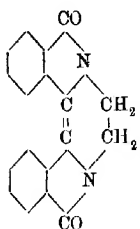


colourless needles, m. p.  $190-191^\circ$ , and to NN'-ethylenediphtalimide (diphtalylethylenedi-imide, Anderlini, A., 1894, i, 490). The former of these is hydrolysed by hot, moderately dilute aqueous potassium hydroxide to NN'-ethylenephthalimidine-o-carboxybenzamide,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} N \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ , colourless prisms, decomp.  $172-173^\circ$  (silver salt,  $C_{18}H_{15}O_4N_2Ag$ , tufts of needles).

When treated with bromine (2 mols.) in glacial acetic acid solution.

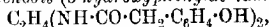
tion, which is then boiled for a few minutes, ethylenedipthalimidine yields a *tribromide*,  $C_{18}H_{16}O_2N_2Br_3$ , unstable, yellowish-brown needles, decomp.  $187^\circ$  (rapidly heated), which is immediately decomposed by water with regeneration of the dipthalimidine. Chlorine does not attack ethylenedipthalimidine in glacial acetic acid or carbon tetrachloride, but in the former solvent together with ethyl ether iodine produces a *di-iodide*,  $C_{18}H_{16}O_2N_2I_2$ , dark brown prisms, m. p.  $180-181^\circ$ .

Ethylenedipthalimidine is converted into diphthalylethylenedimide by boiling with phosphorus pentachloride and phosphoryl chloride, and by heating with sulphur at  $240-250^\circ$  until hydrogen sulphide ceases to be evolved, yields 1:2:4:3-*dibenzoylene*-1:4:5:6-*tetrahydropyrazine* (annexed formula), brownish-orange needles, m. p.  $202-203^\circ$ . This substance, which



is more easily obtained by heating a mixture of phthalide, ethylenediamine, and sulphur in a sealed tube at  $250^\circ$ , is oxidised to diphthalylethylenedimide by chromic and acetic acids.

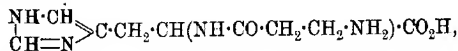
Ethylenediamine (anhydrous or in 50% aqueous solution) reacts vigorously with the lactone of *o*-hydroxyphenylacetic acid (2 mols.), and it is preferable to add alcohol as a diluent; the product is *NN'*-ethylenebis(*o*-hydroxyphenylacetamide),



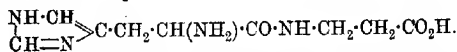
colourless needles, m. p.  $208^\circ$ , which forms a *diphenylurethane*,  $C_{22}H_{20}O_4N_4$ , needles, m. p.  $225^\circ$ . Still more vigorously react 50% aqueous ethylenediamine and the lactone of *o*-hydroxydiphenylacetic acid, and alcohol must be added to keep the reaction under control; the product is *N*-*o*-hydroxydiphenylacetylenebisethylenediamine,  $OH \cdot C_6H_4 \cdot CHPh \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH_2$ , colourless needles, decomp.  $197^\circ$ , whether 1 or 2 mols. of the lactone is present. C. S.

### Histidine and Carnosine. The Synthesis of Carnosine.

LOUIS BAUMANN and THORSTEN INGVALDSEN (*J. Biol. Chem.*, 1918, **35**, 263—276).—The amino-radicle may be removed from carnosine by treatment in aqueous solution with barium nitrite and sulphuric acid. After hydrolysis, by boiling with sulphuric acid, 70% of the theoretical quantity of histidine can be isolated from the deaminised product. Carnosine must therefore be regarded as  $\beta$ -alanylhistidine,



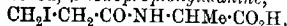
instead of the other possible isomeride, histidyl- $\beta$ -alanine,



This conclusion has been confirmed by the synthesis of carnosine. A solution of  $\beta$ -iodopropionyl chloride in light petroleum is added

slowly to histidine dissolved in water, an alkaline reaction being maintained throughout by the addition of barium hydroxide. The reaction product is not isolated, but after the removal of the barium by means of carbon dioxide, the filtrate is saturated with ammonia, first in the cold and eventually in sealed tubes at 100°. By fractional precipitation with silver nitrate and barium hydroxide, about 3 grams of pure carnosine were obtained from 40 grams of histidine.

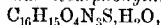
By a similar method, *β*-iodopropionylalanine,



is prepared by the interaction of *α*-alanine and *β*-iodopropionyl chloride. It melts at 153—155°.

Extracts of dog's liver and muscle, which readily hydrolyse certain dipeptides, do not hydrolyse carnosine.

Attempts to prepare histidyl-*β*-alanine, or derivatives of it, have not been successful. By the action of *α*-naphthalenesulphonyl chloride on histidine in alkaline solution, *α*-naphthalenesulphonylhistidine naphthalenesulphonate,  $\text{C}_{26}\text{H}_{23}\text{O}_7\text{N}_3\text{S}_2\cdot\text{H}_2\text{O}$ , is obtained, which melts at 155°, and, on further heating, solidifies, and melts again at 220°. By heating at 150° over phosphoric oxide in a vacuum, the molecule of water is removed, and the anhydrous substance crystallises in long, prismatic rods from methyl alcohol containing a few drops of glacial acetic acid, and melts at 222°. By treatment of its alcoholic solution with sodium hydroxide, the compound yields *α*-naphthalenesulphonylhistidine,



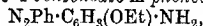
m. p. 236°,  $[\alpha]_D^{25} - 190\cdot8^\circ$ .

Hippuryl-*β*-alanine,  $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2$ , is readily prepared by the interaction of *β*-alanine and hippuryl chloride in alkaline solution. It crystallises in long needles, m. p. 183—185°. H. W. B.

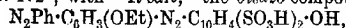
**Crystalline Form of 3:7-Dimethyl-1:9-diethyluric Acid and its Glycol Dimethyl Ether. A Correction.** HEINRICH HILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 255).—The description of the crystalline form of 3:7-dimethyl-1:9-diethyluric acid A., 1917, i, 590) is really that of its glycol dimethyl ether. The former crystallises in small rhombohedra with blunted angles.

C. S.

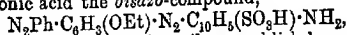
**Azodyes derived from *m*-Phenetidine.** FRÉD. REVERDIN, J.-G. RILLIET, and CAM. VERNET (*Arch. Sci. phys. nat.*, 1918, v], **46**, 74—80).—Benzenediazonium chloride combines with *m*-phenetidine to give 4-benzeneazo-*m*-phenetidine



m. p. 84—85°, yielding a hydrochloride, m. p. 152—153°, an acetyle derivative, m. p. 135°, and a benzoyl derivative, m. p. 146°. This dye, when further diazotised and combined with *β*-naphthol, gives the bisazo-compound,  $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ , brown needles, m. p. 172°, with "R-salt," the bisazo-compound,



a reddish-violet powder, dyeing silk and wool reddish-violet, and with naphthionic acid the *bisazo*-compound,



a blackish-brown powder, dyeing silk a reddish-brown, not fast to light. The base has also been diazotised and combined with 7-amino-1-naphthol-3-sulphonic acid, 1:8-dihydroxynaphthalene-3:6-disulphonic acid, 3-amino-2-naphthol-6-sulphonic acid, 2-naphthol-7-sulphonic acid, 1-naphthol-4-sulphonic acid, and 8-amino-1-naphthol-3:6-disulphonic acid.

Aniline-*m*-sulphonic acid similarly furnishes *m*-sulphobenzenazo-*m*-phenetidine,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_5(\text{OEt})\cdot\text{NH}_2$ , reddish-brown needles, m. p. 214—215°. This base, when further diazotised, combines with *p*-nitrobenzenazo-8-amino-1-naphthol-3:6-disulphonic acid to give the *trisazo*-compound,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_5(\text{OEt})\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})_2(\text{SO}_3\text{H})_2\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  as a blackish-green powder.

In the same manner, *p*-nitroaniline yields *p*-nitrobenzenazo-*m*-phenetidine,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_5(\text{OEt})\cdot\text{NH}_2$ , which, when diazotised and combined with chromotropic acid, gives the *bisazo*-compound,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_5(\text{OEt})\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})_2(\text{SO}_3\text{H})_2$ , a blackish-brown powder, in which the nitro-group may be reduced by sodium sulphide, giving a brown powder, which dyes wool blue. *m*-Phenetidine does not apparently combine readily with diazonium salts of high molecular weight. W. G.

**Influence of Substituents on Reactions. I. The Rate of Reduction of Substituted Phenylhydrazines.** HARTWIG FRANZEN (*J. pr. Chem.*, 1918, [ii], 97, 61—92).—It is already known that derivatives of the aminophenylhydrazines and the ethoxyphenylhydrazines readily undergo fission at the -N-N-linking, the effect being less marked when the substituent group is in the meta-position than when in the ortho- or para-position (Franzen, A., 1907, i, 321; Franzen and Fürst, 1914, i, 206; 1917, i, 58, 59; Franzen and Schmidt, this vol., i, 81). The reduction of substituted phenylhydrazines by stannous chloride and hydrochloric acid appears to be parallel to the above fission reaction in its susceptibility to influence by substituents, but, being more rapid, is more convenient for experimental investigation in the less reactive compounds. Examination of the rate of reduction of phenylhydrazine and its various methyl, chloro-, bromo-, iodo-, carboxylic, and sulpho-derivatives shows that the first four radicles which direct further substituents into the ortho- and para-positions, when in the 2- or 4-position to the hydrazine nucleus, increase the rate of reduction of phenylhydrazine, whereas the last two radicles, which direct further substituents into the meta-position, effect a diminution in the rate of reduction, whether they are in the 3- or 4-position. Radicles of the former class, with the exception of methyl, when in the 3-position likewise increase the velocity of reduction, but the effect is always less than that of the same radicle in the ortho- or para-position, thus corresponding with the observa-

tions already made on the ethoxy- and amino-phenylhydrazines. With the second group of substituents, the influence is always greater in the meta- than in the para-position; the ortho-compounds in these cases were not investigated, because their tendency to ring formation gives rise to complications. With methyl, chlorine, and bromine the influence is greater in the ortho- than in the para-position, but with iodine and ethoxyl the case is reversed. When placed in order of the magnitude of their influence, the relative position of the substituents is  $\text{NH}_2 > \text{OEt} > \text{Me}, \text{I} > \text{Br}, \text{Cl}$ , the substituents methyl and iodine, as also bromine and chlorine, possessing almost equal influence. A striking parallel exists between the tendency of these substituents to facilitate further substitution at the ortho- and para-positions, in which positions of the phenylhydrazine molecule they themselves increase the reactivity of the substance, whilst the class of substituents including the carboxylic and sulpho-groups reduces the tendency of a compound to further substitution, and directs the new group into the meta-position, in which position of the phenylhydrazine molecule they cause the least diminution in the reaction velocity. It is also of interest that the relative effect of the substituents amino, hydroxyl, methyl, chlorine, on the reduction of the aromatic halogen compounds by hydriodic acid falls into a similar order to that above (Klages and Liecke, A., 1900, i, 337). In view of the preceding results, Vorländer's conclusion (A., 1903, ii, 67), that the unsaturated groups in particular possess the power of increasing the reactivity of the substituted compound, is unjustified; this criticism is confirmed by the peculiarity that the nitro-group in 1-chloro-2:4-dinitrobenzene increases the reactivity of chlorobenzene towards ammonia, but not towards hydrogen, whereas the presence of the amino- or hydroxyl group barely affects the former reaction, but favours the latter. The author is of opinion that the increase in the reactivity of phenylhydrazine induced by any such radicle as the amino-group or hydroxyl group is due to the unsaturated nature of the main atom by which it is attached to the benzene ring, and further evidence in support of this view is adduced from the behaviour of 4-hydrazinostilbene, the investigation of which places the  $\text{CHPh}:\text{CH}$ -radicle between  $\text{OEt}$  and  $\text{Me}$  in the above order of influence; the phenyl radicle falls into the same position as the styryl radicle, as is indicated by an investigation of 4-hydrazinodiphenyl. The conclusion is therefore drawn that the series  $\text{NH}_2 > \text{OEt} > \text{Ph}, \text{CHPh}:\text{CH} > \text{Me}, \text{I} > \text{Br}, \text{Cl}$  represents also the relative degree of unsaturation of the radicles concerned, and that the groups  $\cdot\text{SO}_3\text{H}$  and  $\cdot\text{CO}_2\text{H}$ , which effect a reduction in the reactivity of phenylhydrazine, are in an especially saturated condition. On investigation of the reaction of benzyl chloride and its three methyl derivatives with sodium ethoxide, it is found that the case resembles that of phenylhydrazine and the tolylhydrazines, the ortho-derivative being more reactive than the para-compound, and both of these more reactive than the meta-derivative, which indeed is but little more reactive than the parent compound.



Evidence of a similar but less simple nature is supplied by the behaviour of phenyl acetate and the three tolyl acetates towards alcoholic sodium ethoxide, although on account of the presence of water in the commercial alcohol used, the change observed was one of hydrolysis; the relative reactivity of the parent phenyl compound and its three methyl derivatives is identical with that of benzyl chloride and its methyl derivatives.

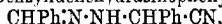
**4-Hydrazinostilbene.**  $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ , was obtained in the form of its *hydrochloride*, pearly leaflets, m. p.  $254^\circ$  (decomp.), from 4-aminostilbene by successive diazotisation and reduction; *benzylidene* derivative,  $\text{C}_{21}\text{H}_{16}\text{N}_2$ , yellow, crystalline powder, m. p.  $208^\circ$  (decomp.); *dibenzoyl* derivative,  $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2$ , colourless leaflets, m. p.  $196^\circ$ . When heated with dilute hydrochloric acid, the base yields 4-aminostilbene, stilbene, ammonia, and nitrogen. 4-Hydrazinodiphenyl under similar conditions yields only 4-aminodiphenyl and ammonia. D. F. T.

**Aminohydrazines. V. *m*-Amino-*p*-tolyl- $\beta$ -benzylhydrazine.** HARTWIG FRANZEN and COLESTIN MONDLANGE (*Annalen*, 1917, **414**, 189—195. Compare A., 1917, i, 58, 59).—This aminohydrazine has been examined in order to ascertain whether the yellow colour and the capacity to form intensely coloured salts exhibited by *o*-aminophenyl- $\beta$ -benzylhydrazine (*loc. cit.*) are general characteristics of such aminophenylbenzylhydrazines.

Benzaldehyde-*m*-nitro-*p*-tolylhydrazone in boiling ammoniacal alcoholic solution is treated with sodium hyposulphite, whereby sodium *m*-amino-*p*-tolyl- $\beta$ -benzylhydrazinesulphonate and benzaldehyde-*m*-amino-*p*-tolylhydrazine are obtained, which are separated by boiling water, in which the former, pale yellow leaflets, m. p.  $211^\circ$ , is insoluble. It is decomposed by boiling *N*/2-sulphuric acid, yielding sulphur dioxide and benzaldehyde-*m*-amino-*p*-tolylhydrazine, which is then converted into phenylmethylbenziminazole and ammonia. Benzaldehyde-*m*-amino-*p*-tolylhydrazine, obtained from the hot aqueous filtrate (above), forms golden-yellow leaflets, m. p.  $167^\circ$ , is converted by cold 10% hydrochloric acid into phenylmethylbenziminazole and ammonia, and in boiling alcoholic solution is reduced by 3% sodium amalgam, yielding *m*-amino-*p*-tolyl- $\beta$ -benzylhydrazine,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , intensely yellow needles, m. p.  $87^\circ$ , which forms yellow solutions in organic solvents and develops in alcoholic solution an intense magenta colour on the addition of a little dilute mineral acid.

C. S.

**Glacial Acetic Acid as a Solvent for Prussic Acid. Benzalhydrazinophenylacetonitrile and some Derivatives.** J. R. BAILEY and R. H. PRITCHETT (*J. Amer. Chem. Soc.*, 1918, **40**, 1230—1235).—Benzylidenehydrazinophenylacetonitrile,



prepared by adding potassium cyanide to a solution of benzylidenazine in glacial acetic acid, forms colourless crystals, m. p.  $114^\circ$

(Adamczewski, *Diss.*, Heidelberg, 1911, records yellow leaflets, m. p. 111–112°), and is converted by concentrated hydrochloric acid into the corresponding amide, m. p. 171° (to a yellow liquid) (Adamczewski, m. p. 165–167° with decomp.). The nitrile and the amide in glacial acetic acid solution are converted by potassium cyanate into *benzylidene carbamylhydrazinophenylacetonitrile*,  $\text{CHPh}\cdot\text{N}\cdot\text{N}(\text{CO}\cdot\text{NH}_2)\cdot\text{CHPh}\cdot\text{CN}$ , rectangular plates, m. p. 228° (decomp.), and the corresponding amide,

$\text{CHPh}\cdot\text{N}\cdot\text{N}(\text{CO}\cdot\text{NH}_2)\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$ , prisms, m. p. 183° (decomp. at 193°), respectively. The latter is converted by boiling 10% potassium hydroxide and subsequent acidification with acetic acid into *1-benzylideneamino-5-phenylhydantoin*,  $\text{NH}\begin{matrix} \text{CO}\cdot\text{N}\cdot\text{N}\cdot\text{CHPh} \\ \text{CO}\cdot\text{CHPh} \end{matrix}$ , crystals, decomp. 245–250°, which loses benzaldehyde by heating with dilute sulphuric acid and yields *1-amino-5-phenylhydantoin*, decomp. 232°. C. S.

**Pekelharing's Pepsin. IV.** W. E. RINGER (*Arch. Néerland. Physiol.*, 1918, 2, 571–593. Compare A., 1917, i, 233; 1916, i, 226).—In his previous experiments, the extent of proteolysis has been measured by the author by precipitating the proteins with tannic acid and estimating the nitrogen in the filtrate. It is now shown that these results are not quite accurate, because the amount of nitrogenous material precipitated by the tannic acid is found to vary considerably according to the concentration of the salts in the solution. The effect of the error is that the descent of the curve illustrating the course of the digestion is really less than has been represented. The former experiments have now been repeated, the concentration of salt being maintained constant. The optimum concentration of hydrogen ions for the digestion of the albumoses by pepsin varies from  $p_{\text{H}}=2.5$  in the case of protoalbumose to 4.1 for deutoalbumose. These results are in harmony with the view that a combination occurs between enzyme and substrate, because the smaller the hydrolytic product, the larger will be the number of particles in solution, and the sooner the moment will arrive (that is, the lower the degree of acidity) at which all the particles of enzyme are combined with particles of substrate, which according to the author constitutes the maximum point in the curve representing the hydrolysis.

The importance of the electrical charge of the protein in determining the course of proteolysis is illustrated by experiments in which the effect is ascertained of the addition of various potassium salts on the digestion of protein by pepsin. The strongly negative ferrocyanide ion inhibits proteolysis to a much greater extent than either the chloride or the sulphate. H. W. B.

**Action of Chymosin and Pepsin. IV. Action of the Enzymes on Sodium Caseinogenate.** OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, 102, 33–77. Compare A., 1915, i, 726, 911).—Two extracts of gastric mucous membrane may show

equal enzymic activity when tested by their power of coagulating milk, and yet show considerable differences in their digesting power on fibrin or white of egg. This want of parallelism is found also when the substrate chosen in each case is caseinogen, and the activity tested first in the presence of alkali and then in that of acid. In the former case, the solutions become opalescent and a precipitate forms, whilst albumoses are produced in considerable amount, and although there does not appear to be direct proportionality between the strength of the chymosin and the time in which the opalescence becomes of a definite degree or the precipitate is just perceptible, or between the quantity of chymosin present and the amount of albumose produced in a given time, yet the relative strengths of two chymosin solutions may be compared in either of these ways. The results can be interpreted most easily by regarding chymosin and pepsin as separate enzymes, and this view is confirmed by the fact that the differences observed between the coagulating and digesting powers of two extracts are exactly paralleled by the differences in their behaviour towards caseinogen in alkaline and acid solutions respectively. Thus, if one of two solutions of equal peptic power clots milk with greater rapidity than the other, then its action on caseinogen in alkaline solution is found to be much more marked and rapid than is the case with the other enzymic solution.

H. W. B.

**Digestibility of Heated and Unheated Caseinogen.** OLOF HAMMARSTEN (*Arch. Néerland. Physiol.*, 1918, 2, 658—663).—When caseinogen is dissolved in water with the addition of the minimum amount of alkali and the solution heated for an hour in an autoclave at about 116°, a small quantity of albumose is formed, whilst the recovered caseinogen is found to be more readily digested than unheated caseinogen by pepsin in the absence of free hydrochloric acid (negative reaction with Congo-red). The inability of heated milk to maintain the growth of young rats (Funk and Macallum, A., 1916, i, 861) cannot therefore be ascribed to an altered structure in the constituent amino-acids of the caseinogen caused by the heating, and resulting in failure of digestion and utilisation in the body. These results indirectly confirm the hypothesis of the existence of thermolabile indispensable accessory substances in milk.

H. W. B.

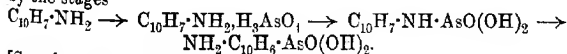
**Influence of Neutral Salts on the Action of the Salivary Diastase.** J. TEMMINCK GROLL (*Arch. Néerland. Physiol.*, 1918, 2, 516—520).—Both the anion and the cation of a neutral salt exert an action on ptyalin, the former being the more potent. The order in which the cations may be arranged expressing their relative activating power corresponds with that in which they affect colloids generally. The order of the anions, however, differs from that which would be expected if the diastase was a simple colloid. Neutral salts affect, therefore, not only the degree of dispersion of the ptyalin, but have another action, depending probably on the colloidal state of the substratum.

H. W. B.

**Enzymes and Surface Action.** W. M. BAYLISS (*Arch. Néerland. Physiol.*, 1918, 2, 621—624).—The action of enzymes consists in the condensation on their surfaces by adsorption of the constituents of the reacting systems, including water. The effect of this concentration is to increase the rate at which the reactions take place and to diminish greatly the time taken for equilibrium to be attained. If the rate of action of an enzyme, such as urease, is a function of the amount adsorbed, the presence of an indifferent substance, which is adsorbed to a greater extent than carbamide, should delay the reaction. Saponin is adsorbed by charcoal to a greater extent than carbamide, and more carbamide is adsorbed by a given weight of charcoal from a pure carbamide solution than from one containing a mixture of carbamide and saponin. Applying these results to urease, it is found that the addition of saponin to a solution of carbamide containing urease delays the rate of action of the enzyme, although eventually the extent of hydrolysis of the carbamide is equal to that attained in the absence of the saponin. Bile salts and amyl alcohol produce similar effects. The inhibiting effect of saponin is greater at a low temperature than at a higher one, and the temperature coefficient of the reaction is increased, both phenomena being in harmony with the view that the saponin exerts its action by adsorption. The author's hypothesis does not seem to account for the specificity of enzymes, but without attempting to disregard this difficulty, he points out that the surface forces controlling adsorption are as yet too little known to warrant a dogmatic statement on this question.

H. W. B.

**Some Naphthalene Derivatives.** A. ARCHIBALD BOON and JAMES OGILVIE (*Pharm. J.*, 1918, 101, 129—130).—When arsenic acid is heated with an arylamine, the latter may undergo oxidation, as in the preparation of magenta, or it may undergo conversion into an arylarsinic acid,  $\text{AsRO}(\text{OH})_2$ , or even a diarylarsinic acid,  $\text{AsR}_2\text{O}_2\text{H}$ . When an intimate mixture of equal parts of  $\alpha$ -naphthylamine and arsenic acid is crystallised from hot water,  *$\alpha$ -naphthylamine hydrogen arsenate*,  $\text{C}_{10}\text{H}_7\cdot\text{NH}_2\cdot\text{H}_3\text{AsO}_4$ , is obtained in long, colourless needles, m. p.  $170^\circ$ , which become purple on exposure to the atmosphere or when heated above  $165^\circ$ ; the apparent molecular weight in alcohol is 156. If this arsenate is heated with four-ninths its weight of  $\alpha$ -naphthylamine at  $200^\circ$  for a short time, 1-aminonaphthyl-4-arsinic acid is produced, together with an amorphous, purple substance,  $\text{C}_{18}\text{H}_{11}\text{ON}$ ; this gives a violet solution in organic solvents, and is doubtless an oxidation product of the naphthylamine. The formation of the arsenate and its further conversion into an arsinic acid confirm the general view that the reaction yielding aminonaphthylarsinic acid occurs by the stages

[See also *J. Soc. Chem. Ind.*, October.]

D. F. T.

### Physiological Chemistry.

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**Estimation of Buffer Effects in Measuring Respiration.** W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, 35, 237—240).—The indicator method of measuring respiration (Haas, A., 1917, i, 433) consists in placing organisms in a solution containing an indicator and observing changes in colour produced by the giving off of carbon dioxide. Since the acidity and colour are affected by substances having a buffer action, it is evident that when such substances are present the amount of buffer action must be measured. This can be done by the apparatus described by the author, which permits the addition of measured quantities of carbon dioxide to known volumes of liquid of which the  $p_H$  values are estimated before and after the addition of the carbon dioxide. H. W. B.

**Estimations of the Tension of Carbon Dioxide in the Alveolar Air by the Henderson-Russel Modification of Haldane's Method, and their Application for Testing the Stimulability of the Breathing Centre.** EUGEN JENNI (*Biochem. Zeitsch.*, 1918, 87, 331—358).—By means of the modification by Henderson and Russel of Haldane's method, it was found that the carbon dioxide tension of alveolar air remained constant over prolonged periods. When the subject of experiment is used to the procedure, the variations amount to but 2—3 mm. of mercury; the method is not, however, well adapted to clinical purposes. In a case of emphysema investigated, the tension of carbon dioxide was high. The method can be employed for testing the irritability of the breathing centre. For inhibition, the drugs morphine and pantopone were employed; both cause marked increase in the tension of carbon dioxide in the alveolar air. The preparation of Pavon-Ciba, in corresponding therapeutic doses, causes little alteration in the tension, and its inhibitory action on the breathing centre is less than that of morphine or pantopone. Alcohol is an excitant of the inhibitory centre in the doses used by the author. S. B. S.

**Narcosis and Oxygen Concentration.** B. VON ISSERUN (*Biochem. Zeitsch.*, 1918, 88, 219—231).—The action of narcotics is independent of the oxygen concentration, and there is no marked difference in their action on tadpoles in water rich and poor in oxygen. During narcosis, the oxygen respiration of tadpole diminishes from 18—40%. Ethylurethane and alcohol in narcotising doses cause the same amount of diminution. Potassium cyanide diminishes oxygen respiration to the extent of 30—40% without producing paralysis. Increased partial pressure of oxygen can increase the oxygen respiration of the tadpoles without inhibiting the action of narcotics; in fact, the oxygen consumption of the animals under deep narcosis in water rich in oxygen is greater

than that of non-narcotised animals in water with the normal amount of oxygen.

S. B. S.

**Estimation of the Methyl Groups attached to Nitrogen in the Blood.** A. KOSSEL and S. EDLBACHER (*Arch. Néerland. Physiol.*, 1918, 2, 625—628).—The application of Pregl's micro-analytical method for the estimation of the methyl groups attached to nitrogen (see Edlbacher, this vol., ii, 336) to blood gives results which indicate that the ratio N/Me ranges in normal blood from about 17 to 20, which corresponds with about 5 methyl groups per 100 atoms of nitrogen present. In a few cases of pathological blood, the ratio is rather higher, reaching to 26 in pernicious anæmia. The coagulated protein of the blood does not contain any methyl attached to nitrogen, whilst the amount in caseinogen is about 0.4%.

H. W. B.

**Properties and Composition of Oöcytase.** GUY W. CLARK (*J. Biol. Chem.*, 1918, 35, 253—262. Compare Robertson, A., 1912, ii, 573).—Preparations of oöcytase, the fertilising and cytolytic substance in mammalian blood sera, have been obtained containing protein as an impurity. On hydrolysis, oöcytase yields hypoxanthine and a pentose, but only a trace of phosphoric acid. The active constituent is destroyed by heat at a temperature between 73° and 80°, and by prolonged contact with alcohol. Oöcytase is neither hæmolytic, bactericidal, nor identical with alexin. The characteristic fertilising and cytolytic properties are probably to be associated with the nucleosidic structure of the oöcytase.

H. W. B.

**Existence in the Animal Body of Substances capable of Fixing Alkaloids.** W. STORM VAN LEEUWEN (*Arch. Néerland. Physiol.*, 1918, 2, 650—657).—Pilocarpine dissolved in rabbit's serum does not excite a strip of intestinal muscle (cat) to the same extent as an aqueous solution of pilocarpine containing the same proportion of the drug. The neutralising effect of the serum only appears slowly, and reaches its maximum in about twenty-four hours. Sera from other animals are not so effective, that from the dog being quite inert. The neutralising action is due to fixation and not to destruction of the pilocarpine, because by suitable means all the alkaloid may be subsequently extracted from the serum and found to retain its original stimulating power in aqueous solution. The neutralising substances are present also in the liver and other organs of the body, and it is to their presence in differing amounts that the varying susceptibility of different animals to alkaloids is probably due.

H. W. B.

**Calcium and Magnesium Metabolism. V. Effect of Acid and other Dietary Factors.** MAURICE H. GIVENS (*J. Biol. Chem.*, 1918, 35, 241—251. Compare this vol., i, 321).—Experiments on two dogs are described, the results of which indicate that the ingestion of either hydrochloric acid or sodium chloride pro-

duces a small increase in the elimination of calcium in the urine, although it does not appreciably affect the calcium balance. The excretion of magnesium is not affected in either case. H. W. B.

**Autolysis of Animal Tissues.** KARL GUSTAV DERBY (*J. Biol. Chem.*, 1918, **35**, 179—219).—Yeast cells and various animal tissues (liver, spleen, pancreas, gastric mucous membrane, and leucocytes of dogs and pigs) all contain two kinds of proteolytic enzymes: (a) pepsin-like enzymes which hydrolyse proteins to peptones, but not further, and for the action of which the optimum hydrogen ion concentration is about  $p_H = 3.5$ ; (b) enzymes similar to trypsin or erepsin, which attack only peptones or peptides, and hydrolyse them to amino-acids. The optimum hydrogen-ion concentration for the latter enzymes is about  $p_H = 7.8$ . In some tissues, one type of enzyme is present to a much greater extent than the other.

Autolysis in the case of the pancreas and the liver proceeds furthest when the  $p_H$  is maintained between 5 and 6, and appears to be due to the action of the above proteolytic enzymes, the maximum action being obtained when the degree of acidity is such that both types of enzymes are able to work simultaneously. Pieces of tissue which have been treated with weak acids and then transferred to an alkaline solution undergo autolysis much more readily than similar pieces placed straightway into the alkaline solution. This is due to the ability of the ereptic enzyme to break down the peptones formed by the peptic enzyme in the acid solution, although it is unable to hydrolyse the native protein. H. W. B.

**Co-ferment of Fermentation in the Animal Body.** II. OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **102**, 1—32. Compare this vol., i, 242).—The co-enzyme of zymase appears to exist in almost all the tissues of the frog and rabbit. It is present in relatively the largest amount in frog's muscle; it is absent from blood-serum. It is most readily extracted by boiling water. Cold water extracts contain the co-enzyme, but an inhibitory substance is also present which is destroyed by boiling. The inhibitory substance exerts its action on zymase and not on the co-enzyme, and appears to be of a protein nature. The chemical properties of the co-enzyme in muscle resemble those associated with the co-enzyme in yeast. It is dialysable, not destroyed by boiling, precipitated by alcohol, adsorbed by charcoal, etc. The course of fermentation, using the muscle co-enzyme, is analogous to that observed when the co-enzyme from yeast is employed.

The respiratory substance (*loc. cit.*) which accelerates the oxidation process in muscle appears to be identical with the co-enzyme of yeast and muscle. A similar co-enzyme is also present in germinating peas. H. W. B.

**The Constituents of Alcoholic Extracts of Organs which are Active in Wassermann's Reaction.** FRITZ SILBERSTEIN (*Biochem. Zeitsch.*, 1918, **88**, 1—12).—Extracts of incompletely

autolysed organs are more active as "antigens" in the Wassermann reaction than are extracts of the fresh organ. If autolysis, however, proceeds too far, the extracts become inactive. Neither the fraction soluble in alcohol, but insoluble in ether (soaps), nor the fractions soluble in alcohol, ether, and acetone (fatty acids, fats, and cholesterol) of either fresh or autolysed livers give a reaction as marked as the whole extract. The fraction from fresh organs containing the lipoids gives as good results as the whole extract of the partly autolysed organ. The best reaction, however, is obtained by a mixture of the lipid fraction with equivalent amounts of the fraction containing the soaps, fatty acids, and cholesterol. Treatment of the organ with trypsin or steapsin destroys its power of giving antigens; this function of the organs is not, however, altered by their treatment with pepsin-hydrochloric acid, ricin-lipase, or with dilute acid or alkali.

S. B. S.

**Biology of Silicic Acid and Aluminium Oxide in Birds' Feathers.** MAX GONNERMANN (*Zeitsch. physiol. Chem.*, 1918, 102, 78—84. Compare A., 1917, i, 494).—Feathers almost always contain silicic acid and aluminium oxide. The amounts vary considerably in different birds, and appear to depend largely on the content of these substances in the food. The largest quantity of silicic acid found was in the feathers of the dove, *Columba palumbus* (77% of the total ash), whilst the feathers of the jay, *Corvus glandarius*, contained the most alumina (2.46%). Apparently, the feathers constitute a storing place for both substances.

H. W. B.

**Relation of the Quality of Proteins to Milk Production.** IV. E. B. HART and G. C. HUMPHREY [with D. W. SMITH] (*J. Biol. Chem.*, 1918, 35, 367—383. Compare A., 1917, i, 608).—Similar experiments to those already described have been carried out, the results of which indicate an approximate equality and efficiency of the proteins of gluten feed and oil meal as supplements to the proteins of corn meal and clover hay, an increased supplementing effect for distiller's grains, and an inferior efficiency for cottonseed meal, taken in relation to the quality and quantity of milk produced.

H. W. B.

**Effect of Heat on the Citric Acid Content of Milk. Isolation of Citric Acid from Milk.** H. H. SOMMER and E. B. HART (*J. Biol. Chem.*, 1918, 35, 313—318).—Citric acid can be obtained from cows' milk, after freeing the latter from fat and protein, in the form of calcium citrate; it is present to the extent of about 0.2% of the milk or 2% of the milk solids. Citric acid is not destroyed or transformed into an insoluble salt by heating the milk even in an autoclave at 15 lb. pressure for one hour. The loss in anti-scorbutic power observed on heating milk is therefore not due to the destruction of citric acid, but to the inactivation of the anti-scorbutic vitamins.



To estimate citric acid in milk, the caseinogen is precipitated by a dilute sulphuric acid solution of mercuric sulphate and the filtrate treated with dilute potassium permanganate solution. The citric acid is oxidised to acetonedicarboxylic acid, which is precipitated by the excess of mercury sulphate. The mercury in the precipitate is estimated by dissolving in hydrochloric acid and titrating with potassium cyanide and silver nitrate, using potassium iodide as indicator. H. W. B.

**Attempt to Filter the Enzymes of Milk.** JEAN PICCARD and MARY RISING (*J. Amer. Chem. Soc.*, 1918, **40**, 1275—1281).—Attempts have been made to sterilise milk by filtration so that it would be free from germs and suspended impurities, while the enzymes would be unchanged. Failure resulted because a filter could not be found with pores large enough to allow the passage through them of the colloidal enzyme without at the same time allowing the passage of bacteria.

In the course of the work it was found that the Schardinger enzyme remains in the liquid portion of the milk after the casein and the fat have been removed by a small amount of acid. If the casein is precipitated by stronger acids, the enzyme is precipitated with it, and by still more acid it is destroyed. C. S.

**Action of Sugars on Bronchial Secretion.** D. LO MONACO (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 103—109).—The fact that the subcutaneous injection of sugars in small doses largely increases, and in larger doses diminishes and may even entirely prevent, lactation in women, cows, goats, etc., and that similar modifications of other animal excretions are also produced in this way, has led the author to examine the effect of subcutaneous injection of sucrose on a patient exhibiting copious bronchial secretion. The injection was rapidly followed by a diminution in the amount of the bronchial secretion, which sometimes ceased completely, re-appearing again when the injections were suspended. This effect of the injection of sugar may be of great importance in removing one of the principal causes of the spread of phthisis, namely, the ingestion and respiration of dried tubercular sputum. T. H. P.

**Decomposition of Muconic and Adipic Acids in the Animal Body.** YOSHITANE MORI (*J. Biol. Chem.*, 1918, **35**, 341—351).—Muconic and adipic acids injected subcutaneously into rabbits are excreted to a large extent unchanged in the urine. H. W. B.

**Formation of the Unsaturated Acids in the Animal Organism. I. Behaviour of *p*-Methoxyphenylpropionic Acid in the Organism of the Rabbit.** IWAO MATSUO (*J. Biol. Chem.*, 1918, **35**, 291—296).—After the subcutaneous injection of *p*-methoxyphenylpropionic acid, anisic and glycyllanic acids were isolated from the urine, instead of the expected cinnamic acid derivatives (compare Dakin, A., 1909, ii, 684). H. W. B.

**Formation of *p*-Hydroxyphenyllactic Acid in the Animal Organism and its Relation to Tyrosine Catabolism.** YASHIRO KOTAKE [with ZENJI MATSUOKA] (*J. Biol. Chem.*, 1918, **35**, 319—331).—When *l*-tyrosine or *p*-hydroxyphenylpyruvic acid is administered to rabbits or men, *l*-hydroxyphenyllactic acid appears in the urine, accompanied occasionally by small amounts of the *dl*-acid. The administration of *dl*-hydroxyphenyllactic acid is followed by the elimination of only the *d*-acid, the levorotatory component being evidently destroyed to a certain extent in its passage through the body.

H. W. B.

**Relation between Nutrition and the Formation of Kynurenic Acid from Tryptophan.** ZENJI MATSUOKA (*J. Biol. Chem.*, 1918, **35**, 333—339).—The rate of formation of kynurenic acid from tryptophan is almost constant in the rabbit, the injection of 1 gram of tryptophan being followed by the elimination of between 0.2 and 0.3 gram of kynurenic acid in the urine. Apparently kynurenic acid is very stable in the animal body, and it cannot take the place of tryptophan for the maintenance of nutrition. The formation of kynurenic acid from tryptophan is not therefore profitable from the point of view of nutrition.

H. W. B.

**The Biological Action of Convolvulin and Jalapin.** G. EINRICH (*Biochem. Zeitsch.*, 1918, **88**, 13—34).—These substances are like the saponins and agaricin in that they exert a hæmolytic action when they are in neutral solution. They are very sensitive to alkalis, however, and rapidly lose the hæmolytic action in the presence of a slight excess of alkali. The hæmolytic action could only be demonstrated in vitro, but not in vivo, as no blood appeared in the urine after intravenous or subcutaneous injection; neither as any purgative action observed. They are both specific poisons to fish. For purgative action, direct contact of the glucosides with the mucous membrane of the intestines is necessary. This action is also lost when the substances are treated with alkali, and the hæmolytic action can therefore be used in testing the value of preparations as drugs. They are less sensitive to the action of mineral acids, as, in spite of the hydrolysis which ensues, the purgative action is not lost. In this respect, they are similar to the saponins. Like the saponins, too, they are only incompletely sorbed in the alimentary tract, and appear unchanged in the feces.

S. B. S.

**The Influence of Temperature on the Capillary Activity of Narcotics.** B. VON ISSEKUTZ (*Biochem. Zeitsch.*, 1918, **88**, 3—218).—Temperature alters the narcotic activity of indifferent narcotics in the same direction as it alters their capillary activity. Increase and decrease of the narcotic activity of the six substances investigated by H. H. Meyer can be ascribed not only to the difference produced in their distribution between water and organic

solvents on warming, but also to increase or decrease of their capillary activity. In the case of other poisons, increase of temperature can cause diminution of capillary activity, whilst their potency is enhanced. S. B. S.

**Combined Action of Narcotics and Potassium Cyanide on Water-fleas.** F. J. J. BUYTENDYK (*Arch. Néerland. Physiol.*, 1918, 2, 521—529).—Warburg's theory of the action of narcotics on living cells is based on the assumption that the narcotic produces a modification in the degree of dispersion of the colloids in the cell. The combined action of two narcotics might be expected to be equal to the sum of the actions of each separately. This is found to be the case when narcotics such as alcohol and chloroform are employed, but not when one of the narcotics is potassium cyanide. Water-fleas live in 3% alcohol or 1.5% urethane for more than twenty-four hours; in a liquid containing 3% of alcohol and 1.5% of urethane, they do not live more than ten minutes. When alcohol and potassium cyanide are similarly tested, it is found that instead of alcohol increasing the toxicity of the cyanide, it actually diminishes it, and the smaller the percentage of alcohol in the mixture, between the limits 3% and  $\frac{1}{2}$ %, the greater is the neutralising effect on the cyanide. It is conceivable that the narcotic might repel the hydrocyanic acid from the surface of the cell, but the author does not consider that an explanation on these lines is adequate to explain the observed facts. Moreover, the author has been unable to detect any similar neutralising action of narcotics on the inhibition by potassium cyanide of the phototropic phenomena observable with the *Daphnida*. H. W. B.

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## Chemistry of Vegetable Physiology and Agriculture

**Anaerobic Culture Volumeter.** ZAE NORTHROP (*J. Ind. Eng. Chem.*, 1918, 10, 624—625).—A glass bottle is closed by a cork through which passes a glass tube extending nearly to the bottom of the bottle and having a small Berkefeld filter fixed to its lower end. The tube has a tap just above the cork, and the upper end of the tube passes through a cork which fits into the neck of an inverted tapped separating funnel. The bottle is provided with a small exit tube plugged with cotton wool. The separating funnel is filled with liquid culture medium, and a quantity of the latter is introduced into the bottle so as to cover the filter. After the filled apparatus has been sterilised, the culture containing gas-forming organisms is pipetted into the stem of the funnel, admitted through the tap of the latter; this tap is then closed, the lower tap opened, and the stem of the funnel plugged with cotton wool.

The gas formed by the organisms collects under pressure in the funnel, and may be transferred to a gas burette for examination.

W. P. S.

**The Influence of Dicyanodiamide on the Growth of various Micro-organisms.** LUISE MÖLLER (*Biochem. Zeitsch.*, 1918, **88**, 85—96).—Experiments were carried out with various wild yeasts, moulds, and bacteria, and these indicate that dicyanodiamide has no advantages as a sole source of nitrogen for organisms; on the contrary, it exerts a deleterious action on their growths.

S. B. S.

**A Study of the Antiseptic Properties of certain Organic Compounds.** I. J. KLIGLER (*J. Exp. Med.*, 1918, **27**, 463—478; from *Physiol. Abstr.*, 1918, **3**, 270—271).—An examination of the antiseptic properties of a number of organic compounds, including dyes of the triphenylmethane series.

S. B. S.

**The Formation of Ferments. VII.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **88**, 35—42. Compare this vol., i, 328).—The conditions for the formation of the catalase of *Proteus* were investigated. Whilst leucine is essential for the formation of urease by this species of bacteria, this is not the case for formation of the catalase. Other amino-acids, such as aspartic acid and alanine, can be employed, and a considerable development of this ferment takes place in a medium containing, besides the essential inorganic salts and one of these amino-acids, sodium lactate. The catalase acts after the bacteria have been killed (that is, in the presence of toluene). If inactivated by not too large quantities of mercuric chloride and too long a period of contact with this substance, its activity can be restored by treatment with potassium cyanide.

S. B. S.

**The General Relationship of Aldehydes to Alcoholic Fermentation. The Co-ferment of Yeast.** CARL NEUBERG (*Biochem. Zeitsch.*, 1918, **88**, 145—204).—The author gives detailed experiments which confirm his previous statement that aldehydes generally accelerate the alcoholic fermentation by yeasts of dextrose and mannose. His experiments include a series of fatty aldehydes from formaldehyde up to decaldehyde, chloral hydrate, hydroxyaldehydes (aldol, acetopropionaldol), unsaturated aldehydes (citronellal and citral), aromatic aldehydes (benzaldehyde, *p*-isopropylbenzaldehyde, phenylacetaldehyde), aromatic hydroxyaldehydes and their ethers (salicylaldehyde, *p*-hydroxybenzaldehyde, anisaldehyde, piperonal, and vanillin, which is the only aldehyde which failed to give acceleration), the unsaturated aromatic aldehyde, cinnamaldehyde, cyclic aldehydes (furfuraldehyde and cyclocitral), dialdehydes (glyoxal, isophthalaldehyde, cephthalaldehyde), keto-aldehydes (methylglyoxal and phenylglyoxal), and aldehyde-acids. The author also confirms his former statement that a mixture of keto-acids with potassium phosphate acts as a co-ferment. He suggests that certain differences in results

on this point obtained by Harden (A., 1917, i, 501) may be due to the fact that the yeast preparations employed by the latter were not quite free from co-ferments. S. B. S.

**Chromogenic Yeasts. New Biological Reaction for Iron.** M. W. BZYERINOK (*Arch. Néerland. Physiol.*, 1918, 2, 609—615).—Several yeasts containing lactase have the property of secreting under favourable conditions a colourless chromogen which, in the presence of a salt of iron and atmospheric oxygen, is converted into a red pigment. The "fat" yeast, *S. pulcherrimus*, which is characterised by its power of forming fat, does not contain lactase, but it nevertheless forms the above colourless chromogen and red pigment more readily and abundantly than any of the other yeasts. Since it occurs frequently on grapes and in heather honey, and can thus be easily obtained, it has been employed by the author for the preparation and examination of the chromogenic substance. If the yeast is grown on an iron-free medium, pigmentation does not occur. On adding a trace of an iron salt and exposing to air, the red coloration gradually appears. Inoculation of the yeast into a medium containing as little as 10 mg. of iron citrate in 100 c.c. is sufficient to cause the developing yeast cells to become surrounded with a pigmented halo, whilst with larger quantities of iron the cells themselves become red.

The pigment has acidic properties, forming colourless salts with strong bases, which when acidified again produce red solutions. It is a stable substance; its solution in dilute sulphuric acid may be boiled without the occurrence of any decomposition. It does not appear to belong to the anthocyanin or the carotinoid group of pigments. H. W. B.

**Anæsthesia and Respiration.** A. R. C. HAAS (*Science*, 1917, N.S., 46, 462—464).—Using a method previously described (compare A., 1917, i, 433) for the estimation of small quantities of carbon dioxide in solution, the author finds that when *Laminaria* is exposed in sea-water to the action of anaesthetics, in sufficient concentration to produce a measurable effect, there is an increase in respiration. This may be followed by a decrease if the reagent is sufficiently toxic. No decrease is observed with low concentrations which are not toxic. W. G.

**Photosynthesis.** W. J. V. OSTERHOUD (*Amer. J. Bot.*, 1918, 5, 105—111).—For the demonstration of photosynthesis, an apparatus is described which permits of the removal, at intervals, of satisfactory samples of the gases by which the leaf is surrounded, of the stirring and mixing of the gases when necessary, and of the analysis of the gases by a simple method which is sufficiently accurate for ordinary purposes. The apparatus is figured in the original. W. G.

**A Simple Method of Measuring Photosynthesis.** W. J. V. OSTERHOUD and A. R. C. HAAS (*Science*, 1918, N.S., 47, 420—422).—Minute amounts of photosynthesis can be accurately measured

by placing aquatic plants, such as *Ulva*, *Spirogyra*, *Hydrodictyon*, and *Potamogeton*, in solutions containing hydrogen carbonates with a little phenolphthalein, and observing the change in the colour of the indicator on exposure to sunlight. The method can be used for quantitative investigations or for demonstration purposes.

W. G.

**Methods of Studying Permeability of Protoplasm to Salts.** S. C. Brooks (*Bot. Gaz.*, 1917, 64, 230—249).—A general discussion of the methods commonly used in the study of permeability, from which the steps most essential to further progress in the solution of the problem are considered to be: (1) an analysis of the various disturbing factors in the methods involving chemical estimations and the satisfactory interpretation of the results obtained by these methods; (2) a similar analysis of the methods depending on turgor, with special reference to the possible effect of exosmosis; (3) the establishment of methods determining progressive changes in permeability without the disadvantages attaching to the methods at present in use. The author considers that his diffusion method (compare following abstract) answers these requirements.

W. G.

**A New Method of Studying Permeability.** S. C. Brooks (*Bot. Gaz.*, 1917, 64, 306—317).—The method described depends on the diffusion of salts or other substances through a diaphragm of living tissue. Two cells are prepared of glass tubing 18 mm. in diameter, one being 2.5 cm. and the other 4 cm. in length, the ends being ground flat. Between these two edges is placed the tissue, and the cells are rapidly filled with the necessary solutions in turn, and the apparatus set up vertically, the longer cell being at the bottom and closed by a rubber tube and clip, and the upper cell covered to prevent loss by evaporation. The permeability, as shown by the rate of passage of salts through the diaphragm, is measured by determining the changes in electrical conductivity of the two solutions. Where dead tissue is required for experiments on the permeability of the intercellular substance, living disks are exposed to an atmosphere saturated with chloroform vapour for sixteen to twenty-four hours. The results obtained with disks of *Laminaria Agardhii* indicate that the protoplasm of this kelp is normally permeable to the salts of sea-water. Sodium salts cause an increase of permeability, which culminates in death. Calcium and lanthanum salts cause a decrease in permeability, followed by an increase, which culminates in the death of the tissue.

W. G.

**Antagonism and Permeability.** W. J. V. OSTERHOUDT (*Science*, 1917, N.S., 45, 97—103).—Experiments show that all substances which affect permeability may be divided into two groups: (1) those which act like sodium chloride, (2) those which act like calcium chloride (compare Brooks, preceding abstracts). It was further found that substances which behave like sodium chloride

with respect to antagonism, in experiments on growth, behave like sodium chloride in their effect on permeability, and similarly for the second group. There is thus a striking parallel between effects on permeability and antagonistic effects in growth, and all solutions which permit normal growth also preserve normal permeability. The author discusses possible theoretical explanations of these facts and gives experimental data in support of his theory. W. G.

**Does the Temperature-coefficient of Permeability indicate that it is Chemical in Nature?** W. J. V. OSTERHOUT (*Bot. Gaz.*, 1917, 63, 317—320).—The results of Stiles and Jørgensen (compare A., 1916, i, 108) indicate that permeability is chemical rather than physical in nature. From a brief, critical survey of their work, and taking into account his own work on the temperature-coefficient of permeability (compare *Biochem. Zeitsch.*, 1914, 67, 272), the author does not accept the view that permeability is chemical in nature. W. G.

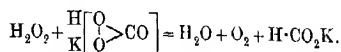
**Similarity in the Effects of Potassium Cyanide and of Ether.** W. J. V. OSTERHOUT (*Bot. Gaz.*, 1917, 63, 77—80).—When potassium cyanide is added to sea-water in which are tissues of *Laminaria Agardhii*, it first causes a temporary decrease in permeability, thus resembling, in this respect, anæsthetics such as ether, chloroform, and alcohol, but the concentrations of potassium cyanide necessary to produce a decrease of permeability are very much smaller than the corresponding concentrations of the latter substances. W. G.

**The Antagonistic Action of Salts.** I. W. H. VAN OYE (*Biochem. Zeitsch.*, 1918, 87, 418—424).—A preliminary account of attempts to correlate physical properties of salts in solution with their biological action. It is shown that chlorine is adsorbed less by various adsorbents from solutions containing sodium, potassium, and calcium chlorides than from a solution of sodium chloride alone. The proportions of the various cations in the experiments were those used by Osterhout in his biological experiments. Experiments are also described on diffusion of chlorine through a dialyser from solutions of sodium chloride alone or mixed with potassium and calcium chlorides. S. B. S.

**The Reduction of Carbon Dioxide by Hydrogen Peroxide as the Basis of Assimilation by Plants.** HANS WISLIZENUS (*Ber.*, 1918, 51, 942—965).—The reduction of carbon dioxide to formic acid, but not to formaldehyde, has been achieved by many chemists, among whom Bredig and Carter have been most successful from a practical point of view (A., 1914, i, 377). It is recognised, however, that there is no resemblance between the powerful agents employed in the laboratory and the forces at the disposal of the green plant. One agent which is always at hand in nature is hydrogen peroxide, and this is to be regarded as the substance which causes the transformation of carbonic acid into formic acid

(compare Kleinstück, this vol., ii, 107). With the exception of the per-acids, carbonic acid is the only carboxylic acid the anhydride and charged or uncharged anions of which have a peroxidic structure, and the mechanism of the formation of oxygen and formic acid is therefore a mutual deoxidation of two peroxides, a reaction which requires no expenditure of energy.

A series of experiments is described which shows that oxygen and formic acid are actually produced when carbonates are left with hydrogen peroxide, the best results being obtained with a saturated solution of potassium hydrogen carbonate and a 10% solution of hydrogen peroxide. The reaction in this case is represented thus:



According to the above view, the process is one which concerns anions, and therefore a formate should be produced around the anode during the electrolysis of a carbonate or hydrogen carbonate, for the peroxidic anion will be in contact with hydroxyl ions. This also has been proved experimentally, and it may be possible to find the most suitable conditions of voltage and amperage to study this anodic, peroxidic, "round-about reduction," as it is called, more thoroughly.

The second stage in the assimilation of carbon dioxide is the further reduction to formaldehyde. This requires energy (light), a special catalyst (chlorophyll), and other factors, and is altogether more difficult of achievement than the first step. J. C. W.

**Influence of certain Organic Substances on the Development of Plants. II.** G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1918, [v], 27, i, 38—42).—Further experiments (A., 1917, i, 244, 681) have been made on the influence on beans, maize, beetroot, tobacco and lupin seeds, and plants of mandelonitrile, benzyl and salicyl alcohols (saligenin); potassium benzoate and salicylate; vanillin, eugenol, and tannin; alanine and asparagine; the potassium derivatives of uric acid and xanthine in comparison with caffeine; pyridine and piperidine in comparison with nicotine, and also quinine, strychnine, and morphine. In the germination experiments, use has been made also of cocaine, atropine, and oil of mustard; galvanised iron germinators were used, the seeds being placed on cotton, covered with filter paper, and moistened with 0.1% solutions of the substances mentioned.

The antithetic relations of mandelonitrile and strychnine are confirmed, and so also is the conclusion that the alkaloids in plants possess some unknown but very definite function, which may be that of vegetable hormones. Just as is the case in animals with which the adrenaline of the suprarenal glands is produced from tyrosine, so different species of plants would transform their original indifferent waste products so as to render them fitted for the specific functions they are to serve.

T. H. P.



**Nitrate and Nitrite Assimilation. XIII. Iron and Oxygen as necessary Agents for the Reduction of Alkali Nitrites by Auto-oxidisable Compounds.** OSKAR BAUDISCH (*Ber.*, 1918, 51, 793—805. Compare A., 1916, i, 699—702; 1917, i, 434).—In the last communication, the important discovery was recorded that when solutions of aldoses or ketoses are boiled with ferrous sulphate and sodium carbonate, dark reddish-violet solutions are obtained, containing iron in "internally-complex" union, which have specific reducing properties. For example, alkali nitrites may be reduced to nitric oxide and ammonia, which is again supposed to involve the hypothetical acid, NOH, as an intermediate stage. It is now shown that the activity of the reducing solution is unaffected by oxygen, which may be freely admitted while the nitrite is being boiled with the agent without preventing the reduction, and that, furthermore, if formaldehyde is added to the mixture, the distillate contains hydroxamic acid, produced according to the equation  $\text{CH}_3\text{O} + \text{NOH} = \text{OH} \cdot \text{CH} : \text{N} \cdot \text{OH}$ .

It is further demonstrated that pentoses, dihydroxyacetone, glycolaldehyde, lævulose, and maltose, in addition to the original dextrose and lactose, have the power of forming complex iron compounds which can reduce nitrites, but not nitrates, or nitrobenzene to aniline. It is not necessary, however, to wait until the iron complex has been made from the carbohydrate; it may be applied in the form of the deep violet-red solution obtained by adding ferric chloride to an alkaline solution of catechol-*o*-carboxylic acid. Using the iron in this form, it may be demonstrated that glycerol, glyceric acid, and mannitol cannot reduce nitrobenzene; in other words, only aldoses and ketoses (in this group of compounds) have the property. If the violet catecholcarboxylic acid complex is boiled with dextrose, the solution becomes more brownish-red, showing that the metal is transferred to the sugar molecule.

Developing the subject further, the author has found that not only aldoses and ketoses, but such compounds as catechol, quinal, pyrogallol, gallic acid, phloroglucinol, quercetin (representing yellow plant pigments), and chrysarobin (representing the anthranols) can reduce nitrites if internally complex iron is present. Now, all these compounds are known to be auto-oxidisable, that is, they take up oxygen and in the presence of water produce hydrogen peroxide (compare Bach, A., 1897, ii, 401; Engler, 1897—1901; Manchot, A., 1900, i, 300). This is an important consideration, for these compounds will only reduce nitrites in the presence of oxygen. For example, if a solution of 1:8-dihydroxy-anthranol (used in cases of psoriasis under the name "cignolin") is boiled with sodium carbonate, a few drops of ferric chloride, and sodium nitrite, no ammonia or nitric oxide whatever passes over in the distillate if the apparatus is first filled with pure nitrogen, but reduction takes place as soon as oxygen is admitted, and ceases again if this gas is excluded once more. Only the sugars are capable of causing the reduction in the absence of oxygen, but

these can provide the necessary oxygen from their own molecules, as Wieland has indicated (A., 1913, i, 1304).

Special experiments emphasise the point again that traces of iron in the "complex" condition must be present. Manganese and copper are without influence. Some of the above polyhydroxyl compounds, like the sugars, can make complexes from iron hydroxides, but not all of them. Phloroglucinol is unable so to "mask" ferric hydroxide, but does make a complex if potassium ferricyanide is provided.

Some theoretical considerations as to these phenomena are offered, and the bearing of them on biochemical processes is mentioned. Particularly important is the power of these auto-oxidisable compounds to bring about oxidations on the one hand (for example, methyl alcohol to formaldehyde) and reductions of nitrites, in the presence of iron complexes, on the other. It is well known that such compounds are widely dispersed in nature—phloroglucinol in many green plants, catechol and quinol in leaf buds, gallic acid, tannin, chrysarobin, yellow pigments, and anthocyanins. It has been shown, furthermore, that the secretion of tanning substances increases when plants are cultivated under less favourable conditions, such as in the cold or dark. In the animal body, also, phenolic compounds with adjacent hydroxyl groups play an important part; for example, adrenaline, and the pigment-forming amino-acid, 3:4-dihydroxyphenylalanine (Bloch, A., 1917, i, 675). Likewise in therapeutics, especially in dermatology, such phenols exert effects that strong reducing or oxidising agents alone are incapable of.

J. C. W.

#### The Distribution of the Aluminium Ion in Plants.

JULIUS STOKLASA [with J. ŠEBOR, W. ZDOBNICKÝ, F. TÝMICH, O. HORÁK, A. NĚMEC, and J. ČWACH] (*Biochem. Zeitsch.*, 1918, **88**, 292—322).—Aluminium is widely distributed in plants. A large number of analyses are tabulated. The xerophytes contain only small amounts of aluminium, whereas the hydrophytes and hygrophilic plants contain relatively large quantities. The mesophytes when growing on dry soils are very poor in aluminium, but contain an appreciable quantity when growing on marshy ground.

S. B. S.

**Direct Influence of the Sap elaborated by the Wild on the Cultivated [Plant], and the Action that Acid Solutions, Directly Absorbed, exert on the Plant.** C. CAMPBELL (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 5—61).—According to Comes, the greater resistance normally shown by wild plants when compared with cultivated ones is due to the greater acidity of the juices of the former. In order to obtain information bearing on this hypothesis, the author has carried out preliminary experiments to ascertain: (1) the influence exerted on a cultivated stock by a wild

graft, and (2) the effect on plants of the direct absorption of acid solutions.

T. H. P.

**Occurrence of Carotin in Oil and Vegetables.** AUGUSTUS H. GILL (*J. Ind. Eng. Chem.*, 1918, 10, 612—614).—Carotin was found to be present in maize, squash, orange-peel, flax seed, mustard seed, black sesame seed, butter, tallow, palm oil, and grass, but not in rape seed, white sunflower seed, turnip, safflower, cotton seed, or turmeric.

W. P. S.

**Chemical Investigations on *Elaphomyces hirtus*.** G. ISSOGLIO (*Gazzetta*, 1917, 47, ii, 31—48).—Analysis of *Elaphomyces hirtus* shows that it contains a *microsterol*,  $C_{30}H_{54}O_2$ , crystallising in silky, white needles, m. p.  $265^{\circ}$ ; traces of unidentified alkaloids; mannitol; microinulin, which gives no coloration with iodine and does not reduce Fehling's solution; paraisodextran, extractable by dilute alkali solution and coloured reddish-brown by iodine; fungin, containing 2.28% of nitrogen. The spores contain a brown pigment with 5% of nitrogen.

T. H. P.

**Carbohydrates in Mulberry Leaves.** SÖJIRÖ KAWASE (*Journ. Tokyo Chem. Soc.*, 1918, 39, 245—294).—The carbohydrates in mulberry leaves are dextrose, lævulose, sucrose, starch, dextrin, araban, galactan, and cellulose. Of these, cellulose occurs in largest amount, next comes a viscous substance consisting of araban and galactan, whilst starch is present in relatively small amount. The nutriment for the silkworm is therefore not starch as is generally supposed. The viscous substance in the leaves does not contain albuminous matter. The changes in the amounts of carbohydrates in the leaves during the development of the plant, or according to the time of gathering the leaves, or during the drying after gathering were determined, and are discussed from the physiological point of view.

S. H.

**Biochemistry of Sea Weeds.** HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1918, 101, 236—247. Compare A., 1915, i, 931).—Various kinds of algæ have been examined for the presence of soluble carbohydrates and laminarin. Of eight species of brown algæ, two, *Desmarestia aculeata* and *D. viridis*, contained laminarin, whilst in all the percentage of soluble carbohydrates was small. Four species of *Florideæ* were found to contain trehalose, but not mannitol. Of the *Chlorophyceæ* investigated, *Cladophora rupestris* contained 15% of soluble carbohydrates, including saccharose, and a lævorotatory polysaccharide resembling inulin.

H. W. B.

**Isolation and Identification of Stachydrin from *Lucerna* Hay.** H. STEENBOCK (*J. Biol. Chem.*, 1918, 35, 1—13. Compare A., 1917, i, 439).—A full account of work previously published.

H. W. B.

## General and Physical Chemistry.

### Comparative Study of the Flame and Furnace Spectra of Iron. G. A. HEMSALECH (*Phil. Mag.*, 1918, [vi], 36, 209—230).

A direct comparison has been made of the flame and furnace spectra of iron by the use of the same dispersion apparatus in the two series of observations. In the production of the furnace spectrum, finely divided oxide of iron was introduced into an electrically heated carbon tube by means of a current of air which had previously passed through a glass bulb enclosing an arc burning between iron electrodes.

The furnace spectrum makes its appearance at about 1500°, and at this temperature the spectrum is the same as that obtained with an air flame burning in coal gas. Up to about 2400°, the flame spectra are identical with those given by the furnace at corresponding temperatures. This identity suggests that the cause of the emission is the same under the different conditions obtaining in the two series of observations, and the author supposes that the spectrum is directly due to the thermochemical dissociation of iron compounds. Above 2500°, the furnace spectrum undergoes a radical change, and it is supposed that this is due to the electrical conduction of the vapour.

In contrast with the above parallelism between flame and furnace spectra, it is noteworthy that the iron spectrum emitted by iron in the inner cone of an air-coal gas flame, the temperature of which is less than 1700°, contains lines which are entirely absent from the flame or furnace spectrum up to 2500°. Some of these lines are shown very feebly by an oxy-acetylene flame at a temperature of about 2700°, but their intensity is very much less than that of the lines in the explosive region of the air-coal gas flame. This anomaly in the behaviour of the low temperature Bunsen cone is attributed to the affinity of iron for nitrogen, with the formation of a nitride. The cause of the emission is accordingly chemical, and the chemical excitation at a comparatively low temperature is equivalent to that produced by thermochemical excitation at a very much higher temperature. In its development, the cone emission approaches, in fact, that of the self-induction spark.

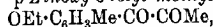
H. M. D.

### Spectrochemical Notes. I. Polyketo-compounds. II. Olefins and Ketenes. III. Spectrochemical Practice. K. von AUERS (*Ber.*, 1918, 51, 1116—1133).—I. This section discusses the influence of the introduction of conjugated carbonyl groups in a compound on the refraction and dispersion. As the subjoined table shows, the simple conjugation $-\text{CO}\cdot\text{CO}-$ causes unimportant alterations, which are not much more marked when further

carbonyl groups are introduced, but conjugations with an ethylene linking of the types  $-C:C:C:O$ , and especially  $-C:C-CO-CO-$ , cause very considerable exaltations in refraction and dispersion.

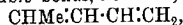
Formula.	$E\sum_{\alpha}$ .	$E\sum_{\beta}$ .	$E\sum_{\beta}-\sum_{\alpha}$ .	$E\sum_{\gamma}-\sum_{\alpha}$ .
$CH_3CO\cdot COMe$ .....	+0.42	+0.41	+9%	—
$CO_2Et\cdot CO_2Et$ .....	0.27	0.27	4%	4%
$CH_3CO\cdot CO\cdot CO_2Et$ .....	0.60	0.60	—	—
$CO(CO_2Et)_2$ .....	0.57	0.56	10%	—
$C_6H_5(CO_2Et)_2$ .....	0.68	0.68	—	—
$C_6H_5CO\cdot COMe$ .....	1.01	1.05	—	—
$COPh\cdot CO\cdot COMe$ .....	1.37	1.45	—	—
$(p)OMe\cdot C_6H_4Me\cdot CO\cdot COMe$ ..	1.27	1.35	80%	—
$(p)OEt\cdot C_6H_4Me\cdot CO\cdot COMe$ .....	1.46	1.53	78%	—
$C_6H_5CO\cdot CO_2Et$ .....	0.89	0.94	46%	52%

Most of the above compounds are already well known, but complete physical data are recorded in each case, for which the original should be consulted. *p*-Ethoxy-*o*-tolyl methyl diketone,



appears to be new. It crystallises in glassy prisms, m. p. 63–64°, has  $D_4^{20}$  1.0524,  $n_D$  1.50733,  $n_D$  1.51270,  $n_D$  1.52888, at 65°, and is prepared as follows. *o*-Propionyl-*p*-cresol is ethylated by means of ethyl sulphate, the *p*-ethoxy-*o*-tolyl ethyl ketone, m. p. 50–51°, is treated with amyl nitrite and hydrochloric acid, and the oxime, m. p. 105–106°, is hydrolysed by boiling sulphuric acid.

II. In this chapter, it is shown that compounds with cumulated ethylene linkings exhibit considerable exaltations in refraction and dispersion. For example,  $\alpha\alpha$ -dimethylallene,  $CHMe_2\cdot C:CH_2$ , b. p. 39–40.5°, has  $E\sum_{\alpha} + 0.60$ ,  $E\sum_{\beta}$  0.59,  $E\sum_{\beta} - \sum_{\alpha} + 21\%$ ,  $E\sum_{\gamma} - \sum_{\alpha}$  18%. This is contrary to Brühl's rule (*Ber.*, 1907, 40, 1160), but is supported by the results obtained by Mereschkowski with *s*-tetramethylallene and  $\alpha\alpha$ -diethylallene (*A.*, 1914, i, 369). The influence of adjacent pairs of ethylene linkings is by no means so great as that of conjugated double bonds, however; piperylene,



for example, has  $E\sum_{\alpha} + 1.81$ ,  $E\sum_{\beta}$  2.10,  $E\sum_{\gamma} - \sum_{\alpha} + 53\%$ .

Ketens have a similar system of cumulated double bonds  $-C:C:O$ , but this system has no special optical influence, as the following table shows:

Formula.	$E\sum_{\alpha}$ .	$E\sum_{\beta}$ .	$E\sum_{\beta}-\sum_{\alpha}$ .
$Ph_2C:O$ .....	+0.91	+1.00	—
$Ph\cdot C:CH_2$ .....	0.88	0.95	—
$Ph\cdot C:C:O$ .....	0.86	0.92	—
$Et_2C:C:O$ .....	-0.08	-0.09	-2%

The polymeride of diethylketen, namely, 1:1:3:3-tetraethylcyclobutan-2:4-dione, has  $E\sum_{\alpha} + 0.27$ ,  $E\sum_{\beta} + 0.25$ ,  $E\sum_{\gamma} - \sum_{\alpha} + \frac{1}{2}\%$ ,  $E\sum_{\gamma} - \sum_{\alpha} + 1\%$ , the increments being of the order normally associated with the four-membered ring system.

III. For the determination of the density of molten substance the author recommends an ordinary pycnometer with a portion of

one of its capillaries, about 2 cm. long, graduated in millimetres. Such an instrument is calibrated for different points along this scale, and in an actual determination the position of the liquid in the tube is noted.

J. C. W.

**Effects of Ring Closure on Spectrochemical Properties. I. Saturated Iso- and Hetero-cyclic Compounds, Unsaturated Isocyclic Substances, and the Question of the Constitution of Benzene.** K. VON ADWERS (*Annalen*, 1918, 415, 98—168).—The author surveys a large field of material, and arrives at the following generalisations. Compounds the molecules of which contain one or more rings (isocyclic or heterocyclic) without linkings of any kind are optically normal; only when the ring is under tension do the molecular refraction and dispersion exhibit exaltation or depression. The spectrochemical character is unchanged when a saturated side-chain closes to form a ring; for example, the pairs *o*-tolyl methyl ether and coumaran and *o*-tolyl ethyl ether and chroman are optically identical, and the same holds for a large number of other coumarans and phenolic ethers. The closure of an unsaturated side-chain to a ring causes a weakening of the optical properties, which is the more pronounced the more unsaturated is the chain; for example, styrene derivatives and indene derivatives, acyclic dienes and cyclic dienes, and acyclic trienes and cyclic trienes. Alkyl groups and other substituents produce an effect opposed to that of ring closure in unsaturated compounds. Exceptions occur to all these generalisations.

Contrary to earlier views, double linkings in open and in closed chains are not optically equivalent, the spectrochemical effect of cyclic double linkings being quite generally slighter than that of ethylenic linkings.

The two physico-chemical methods of investigation, spectrochemistry and thermochemistry, both decide against the view that benzene and its hydrogenated derivatives are different in their innermost structure, and all the physical and chemical facts ally themselves best to a benzene formula containing three double linkings.

The densities and refractive indices of a number of compounds have been redetermined, and new determinations have been made in the case of a large number of coumarans, chromans, phenolic ethers, ketones, and indene derivatives.

The following substances are new: *as-m-xylyl ethyl ether*, b. p. 12—203°,  $D_4^{25}$  0.9487,  $n_D$  1.50297,  $n_D$  1.50692,  $n_D$  1.51874, 1.52872 at 13.95°; *5-bromo-o-tolyl ethyl ether*, b. p. 238—240°,  $n_D$  1.3592,  $n_D$  1.54387,  $n_D$  1.54858,  $n_D$  1.56186,  $n_D$  1.57332; *ethoxy-m-toluic acid*, needles, m. p. 200—201°, and its *ethyl ester*, b. p. 274—275°,  $D_4^{25}$  1.0618,  $n_D$  1.51443,  $n_D$  1.51908,  $n_D$  1.53259, 1.54428 at 15.1°; and *1-methyl-ac-tetrahydro-a-naphthol*, colourless leaflets, m. p. 88—89°.

C. S.

**Quinone-imide Dyes. \*X. Absorption Spectra of the Simplest Triphenylmethane Dyes.** F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, 51, 915—922. Compare this vol., i, 311).—Tables are given which record the shades of colour and absorption spectra of the various series of salts of triphenylcarbinol, its mono-, di-, and tri-amino-, and mono-, di-, and tri-dimethylamino-derivatives, the substituents being in the para-positions. It is shown that the highest salts in all cases, ranging from the di-acid salt of triphenylcarbinol to the tetra-acid salts of magenta and crystal-violet, and obtained by dissolving the dyes in concentrated sulphuric acid, give pure yellow solutions with practically the same absorption band, beginning at about  $\lambda$  480—490  $\mu\mu$ . J. C. W.

**Quinone-imide Dyes. XI. Absorption Spectra of some Amino-derivatives of Naphthaphenazoxonium.** F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, 51, 923—928).—The absorption spectra of some amino-derivatives of 7:12-naphthaphenoxazine and their salts are recorded by tables of curves. The 5-amine is lemon-yellow and gives orange-yellow mono-acid salts and dark blood-red di-acid salts, all having the para-quinonoid configuration. The 9-amine is orange-yellow and gives magenta-coloured mono-acid, greenish-blue di-acid, and bluish-violet tri-acid salts. The 5:9-diamine is orange-coloured, and its salts are as follow: mono-, violet-blue with red fluorescence; di-, orange-yellow; tri-, dark blood-red. The 9-dimethylamino-derivative forms violet mono-acid and green diacid salts. J. C. W.

**Action of Light on Crystals.** FRITZ WEIGERT (*Zeitsch. Elektrochem.*, 1918, 24, 222—237).—The extinction of crystals and the phototropic changes occasioned by light of short wave-length have been examined in the case of  $\beta$ -tetrachloro- $\alpha$ -ketonaphthalene. It is shown that no changes, other than the characteristic colour changes, are brought about in the crystallographic properties of  $\beta$ -tetrachloro- $\alpha$ -ketonaphthalene by the action of light of short wave-length. The axial ratio remains constant even under strong illumination. The absorption spectrum of the crystals varies very much with the electric vector of the entering plane polarised light. When the crystal is not excited, two absorption bands, 395  $\mu\mu$  and 375  $\mu\mu$ , are observed if the entering ray is vibrating in the direction of the  $c$ -axis, but if the entering ray is vibrating in the  $a$ - $b$ -plane, an end absorption at 420  $\mu\mu$  is observed. With excited crystals and the entering light in the  $c$ -direction, there is no change in the absorption spectrum, whilst in the  $a$ - $b$ -plane the absorption is much greater, and an absorption band appears in the yellow-green; this is due to the phototropic colouring. The absorption spectrum of the solutions of  $\beta$ -tetrachloro- $\alpha$ -ketonaphthalene in ether and benzene shows no characteristic bands, but in the long wave-length ultra-violet two obvious steps appear in the same positions as the bands observed with the crystals. Hence it appears that the solid and dissolved molecules are identical. The effect for an equal

quantity of energy when the electric vector is in the *c*-direction is greater than when it is in the *a-b*-plane, since the absorption is greater in the first case than in the second. The lighting up of the crystal by plane polarised yellow light only occurs when the electric vector vibrates in the *a-b*-plane. The maximum excitation of  $\beta$ -tetrachloro- $\alpha$ -ketonaphthalene will therefore only occur when plane polarised light swinging in the *c*-direction is allowed to fall on it, since in this case the light produces no brightening in the opposite direction. The fact that the coloration does not occur in the solution, but only in the crystal, shows that the ordered, closely packed orientation of the molecules in the crystal is the cause of the effect. The two possible formulæ for  $\beta$ -tetrachloro- $\alpha$ -ketonaphthalene are considered in the light of the present results, and it is shown that one only is in accord with them, namely, that with  $\text{Cl}_2$  in the  $\alpha$ -position. J. F. S.

**Temperature-coefficients of the Action of Light on the Chlorine-Hydrogen Mixture with Monochromatic Light.**

M. PADOA and C. BUTIRONI (*Gazzetta*, 1917, 47, ii, 6—9).—The velocities of the combination of hydrogen and chlorine at 10°, 20°, 30°, and 40°, and for lights of different wave-lengths, have been measured, the mean temperature-coefficients being as follows: white light, 1.29; green ( $\lambda=550-530$ ), 1.50; blue ( $\lambda=490-470$ ), 1.31; violet ( $\lambda=460-440$ ), 1.21; ultra-violet ( $\lambda=400-350$ ), 1.17.

T. H. P.

**History of Substances Sensitive to Light.** BORUTTAU (*Zeitsch. angew. Chem.*, 1918, 31, 139—140).—The discovery of the colour change of silver salts under the influence of light is stated to be mentioned first by Konrad Gessner in 1565 in his work, "De omni verum fossilium genere libri aliquot," and not by Fabricius, as erroneously supposed. Gessner describes the darkening of natural hornsilver when exposed to light. The later history of the subject is traversed.

H. J. H.

**The Parent-substance of Actinium, a New Radioactive Element of long Life-period.**

OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1918, 19, 208—218. Compare Soddy, Cranston, and Hitchens, this vol., ii, 211).—The history of the long search for the parent of actinium is detailed. The value for the half-period of actinium itself, given provisionally by Mme. Curie as of the order of thirty years, has been confirmed for an actinium preparation studied during seven years, as well as for several more recently prepared specimens. Early attempts to detect the parent of actinium in uranium salts led to no result. In the first successful experiment, 21 grams of powdered pitchblende were treated with hot concentrated nitric acid. Part of the undissolved siliceous residue, mixed with some mg. of potassium tantalum fluoride, was treated with hydrofluoric acid, which dissolved it for the most part, and the solution, after filtration and evaporation, was



evaporated with concentrated sulphuric acid. Concentrated nitric acid dissolved most of the residue. The undissolved part was mounted on an aluminium sheet (Prep. I), and was found to give  $\alpha$ -rays, which remained constant for some weeks and then slowly increased when the preparation was tested bare. Tested so as to cut out the  $\alpha$ -rays of low range, the growth of the radiation was much more marked, increasing some sixfold in the course of a year, the growth being linear with the time after the first few weeks. This indicated that the siliceous residues from pitchblende contained the sought-for parent of the actinium, resembling tantalum in chemical character and giving  $\alpha$ -rays of low range in producing actinium, the products of which give  $\alpha$ -rays of long range.

This view was completely confirmed by working with larger quantities of rich pitchblende residues obtained from the Chininfabrik, Brunswick. These residues, after a preliminary treatment with hydrochloric acid in presence of a few mg. of tantalic acid, and after the addition of a few mg. of thorium nitrate, were treated as detailed for Prep. I. The rapid growth of the more penetrating  $\alpha$ -radiation was confirmed, and the growth of an active deposit also found. After three weeks, no active deposit could be detected, but after five months an easily measurable quantity was found, and its growth thereafter could be followed and the active deposit itself shown to be that of actinium. The growth of the actinium emanation with time was also observed. For the measurement of the range of the  $\alpha$ -rays and the quantitative study of the growth of emanation and active deposit, preparations were worked up by Giesel at the Chininfabrik from 1 kilogram of pitchblende residues by the method described. The weight was reduced to 16 grams, and from this 73 mg., mainly tantalic acid, was obtained as a white powder, one thousand times as active as the material from which it was separated, and weight for weight forty-six times as active as uranium oxide. Assuming that 8% of the uranium atoms disintegrating produce "protoactinium," the quantity in the 73 mg is that in equilibrium with 86 grams of uranium.

Concordant measurements of the range of the  $\alpha$ -rays gave 3.314 cm. in air at 0° and 760 mm. (wrongly given in the summary and elsewhere as 3.14 cm.). From the Geiger Nuttall relation using the values for the constants  $A$  and  $B$  deduced from observations of the range of the  $\alpha$ -rays of radio-actinium, the calculated half-life period is 180,000 years, but using the values found for the  $\alpha$ -rays of actinium- $X$ , the half-period calculated is 1200 years. It is of interest that in the latter research, Meyer, Hess, and Paneth observed for actinium itself a very feeble  $\alpha$ -radiation of range 3.38 cm., which was probably due to admixed proto-actinium.

Using 45 mg. of the preparation, the growth of the actinium emanation was followed for 100 days, in which time the amount increased to thirty times that present at the first measurement four days from preparation. After the initial period of gradually increasing rate of growth, extending over forty days, due to the successive generation of radio-actinium and actinium- $X$ , the growth

continued linearly with the time. The growth of the active deposit from 9.5 mg. of the preparation was also followed. The active deposit showed a sevenfold increase between the first and the third month.

Protoactinium is one of the five new radio-elements occupying a place in the periodic table hitherto vacant, and the determination of its spectrum and atomic weight should be practicable. For each 1 gram of radium in uranium minerals there should be 60 mg. of protoactinium if its life is 1200 years and 9 grams if its life is 180,000 years. Its atomic weight is either 230 or 234, according as the actinium series is derived from uranium-II or uranium-I, and the former is indicated according to the Fajans generalisation, between atomic weight and life-period of isotopes, which makes the most probable value for the atomic weight of radioactinium 226. Its separation in quantity from pitchblende residue should enable purer preparations of actinium to be prepared than have yet been got, analogously to the preparation of radiothorium from old mesothorium preparations. It should prove to be a radioactive substance, the  $\alpha$ -activity of which increases sixfold during the lapse of some generations and then remains constant and permanent.

F. S.

#### The Life-period of Radiothorium, Mesothorium, and Thorium. LISE MEITNER (*Physikal. Zeitsch.*, 1918, 19, 257–263).

—Measurements extended over seven years of  $\alpha$ -,  $\beta$ -, and also  $\gamma$ -rays of six preparations of radiothorium prepared by electrolytic and chemical methods all gave quite linear logarithmic decay curves, the half-period for the six preparations varying between 30 and 698 days, the mean being 696 days = 1.905 years, accurate to about 1%.

The life-period of mesothorium-I was determined by a new method from the growth of radiothorium from mesothorium initially quite free from radiothorium. Mesothorium as free as possible from radium was prepared from mantle-ash by the firm of Knöfler and Co., Plötzensee, the preparation being crystallised three times at fortnightly intervals to remove radiothorium and its products. Tested for radium, it was found that only 0.8% of the  $\beta$ -rays and 0.62% of the  $\gamma$ -rays were due to this element, which was corrected for. By comparing the curve obtained with theoretical curves drawn for various periods of mesothorium, the results were found to agree well with a value 6.7 years for the half-period. This new value was checked by observation of the decay of the activity of a preparation of mesothorium, prepared by Hahn in 1906 and 7.1 years old at the commencement of the measurements. The period again found, 6.7 years, is considerably higher than the value, 5.5 years, for the half-period of mesothorium commonly accepted. The maximum of the  $\alpha$ -activity of a mesothorium preparation is calculated to be 4.83 years from preparation; and of the  $\gamma$ -rays, through 5 cm. of lead, 3.34 years. For preparations of equal  $\alpha$ -activity of radium and radiothorium respectively in equilibrium with their

$\alpha$ -ray products, the  $\gamma$ -rays of radium are 1.5 times those of radiothorium and 0.9 times those of radiothorium and mesothorium in equilibrium.

The life-period of thorium was calculated by a somewhat elaborate method depending on a comparison of the  $\alpha$ -rays of radium and thorium preparations under defined conditions, and found to be  $2.37 \times 10^{10}$  years (period of half-change), which is somewhat greater than previous estimates—1.28 (Geiger and Rutherford), 1.86 (McCoy),  $1.5 (\times 10^{10})$  years (Heiman). The above value is reduced to  $2.16 \times 10^{10}$  years if the just published value for the half-period of radium is taken as 1580 years (Hess and Lawson). F. S.

**Radioactivity in Natural Sardinian Materials, with Minerogenetic Particulars.** AURELIO SERRA (*Gazzetta*, 1917, 47, ii, 1—5).—A Sardinian porphyritic granite is found to be radioactive, its activity being  $a=0.00010$ . The activity is shown to be due to the presence in the rock of uraniferous biotite; the biotite has been subjected to the action of water which has previously traversed strata of uraniferous mica, the thickness of the latter determining the greater or less radioactive power. T. H. P.

**Abnormality of Strong Electrolytes. II. Electrical Conductivity of Non-aqueous Solutions.** JNANENDRA CHANDRA GHOSH (T., 1918, 113, 627—638).—In a previous paper (compare this vol., ii, 215) it has been shown that the variation of the conductivity of aqueous solutions of salts with dilution can be satisfactorily accounted for by equations which the author has derived from certain assumptions relative to the nature of electrolytes. It is now shown that these equations may be applied with equal success to the conductivity of non-aqueous solutions of strong electrolytes. In all, some thirty different solvents have been examined with reference to the influence of dilution on the conductivity of one or more dissolved electrolytes.

The behaviour of Walden's "normal electrolyte" (tetraethylammonium iodide) can only be explained on the assumption that it at first undergoes polymerisation and then ionises as a ternary electrolyte in accordance with the equation  $(\text{NEt}_4\text{I})_3 = 2\text{NEt}_4^+ + \text{I}_3^-$  or  $(\text{NEt}_4)_3 = (\text{NEt}_4)_3^{\bullet} + 2\text{I}^-$ .

From his observations on the conductivity of tetraethylammonium iodide in different solvents, Walden found that the product of the dielectric constant ( $D$ ) and the cube root of the dilution ( $V$ ), for which the degree of ionisation has a common value, is the same for all solvents. In other words,  $D\sqrt[3]{V}$  is independent of the nature of the solvent. It is shown that this empirical relation follows at once from the author's equations, in which  $\mu_r/\mu_\infty$  represents, however, the activity coefficient and not the degree of ionisation in the Arrhenius sense. H. M. D.

**Electromotive Behaviour of Oxygen and its Anodic Evolution below the Reversible Oxygen Potential.** G. GAURNE and B. DULK (*Zeitsch. Elektrochem.*, 1918, 24, 237—248).—With

the object of ascertaining the nature of the process occurring on an anodically polarised platinum electrode during the evolution of oxygen, the authors have measured the oxygen potential on such an electrode which at the same time is polarised by a measured direct current and an alternating current. The latter acts in the same way as a depolariser of measured strength. Series of measurements are recorded for alternating currents up to 4.0 amperes and current densities up to 0.287 ampere per sq. cm. All measurements were made at 20° and in 2*N*-sulphuric acid. A further series of measurements is recorded for *N*-sodium hydroxide for depolarising currents up to 5.0 amperes and 0.358 ampere per sq. cm. current density. It is shown that the depolarising action of the alternating current is due to the reduction of a platinum oxide by the cathodic component. If the alternating current is slowly increased in strength along with a steady direct current, the oxygen potential (that is, the anode potential) falls below the value for the reversible formation of oxygen. The potential curve obtained from the measurements falls into three parts which are separated by inflection points. The highest of these curves corresponds with  $e_k = 2.0 - 1.5$  volts, the next to  $e_k = 1.5 - 1.23$  volts, and the lowest with  $e_k = 1.23 - 1.0$  volts. This compels the assumption that the electromotive activity of oxygen above its equilibrium potential causes the formation of two different platinum oxides. The oxide which is active over the region  $e_k = 2.0 - 1.5$  volts is unknown and is higher than  $\text{PtO}_3$ . In the region  $e_k = 1.5 - 1.23$  volts, the dissolved oxide  $\text{PtO}_2$  brings about the evolution of oxygen, whilst below 1.23 volts the evolution of oxygen is due to the reaction  $\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{H}_2\text{O} + \text{O}_2$ . The hydrogen peroxide necessary for this change is produced by alternating current on the anode. The most probable value for the oxygen potential is given as  $e_k = +1.23$  volts.

J. F. S.

**Kinetics of Reactions with Electrolytes in Homogeneous Systems.** RUD. WEGSCHEIDER (*Monatsh.*, 1918, 39, 15-86).—A theoretical paper in which the kinetics of the various types of reactions with electrolytes are discussed. Replaceable electrolytes are characterised as those which have the same type of formulae, are not ionised in stages, have the same dissociation constant, have either a common ion and only one unlike ion, or are binary electrolytes. In the case where all the electrolytes are replaceable, it is shown that they have the same degree of dissociation, and this depends on the total concentration of the electrolytes only. With electrolytes having dissimilar ions, the degree of dissociation does not depend on the electrolyte, but on the nature of the ion-forming radicals. If in a reaction only non-electrolytes and replaceable electrolytes are present, then the degree of dissociation does not change if the total concentration of the electrolytes does not change. In general, the course of an electrolytic reaction is different in accordance with whether a separation of electrolyte occurs or not. A statement is evolved which represents the change in dissociation of a non-replaceable electrolyte, in the presence of

replaceable electrolytes, during the course of a reaction with constant total ion concentration. The relationship between the velocity constant, as obtained from the law of mass action, and the course of the reaction is examined for the case where only one electrolyte is active (1) as relating to the undissociated molecule, and (2) either as relating to all the ions or only to one ion of a given molecule. The case of simultaneous reactions with a single electrolyte, and reactions with two electrolytes are also considered. The regularities found in these cases are illustrated by means of well-investigated reactions. In the case of the barium catalysis of Abel and the cation catalysis of Holmberg, it is shown that the formulæ obtained are quantitatively accurate, despite the presence of strong electrolytes. It is clearly shown that the electrolytic dissociation theory is not only not disproved by chemical kinetics, but is strongly supported. Further, the view of the overwhelming importance of the ionic condition in bringing about chemical reactions must be very much restricted. It is also shown on what conditions the divergencies from the laws of chemical kinetics depend, and also how the sensitiveness of kinetic calculations depends on uncertainty of the value of the degree of dissociation.

J. F. S.

**Electrochemical Behaviour of Molybdenum and some Molybdenum Compounds.** KUNO WOLF (*Diss. Tech. Hochschule Aachen*, 1918, 38 pp.; from *Chem. Zentr.*, 1918, i, 608—609).—For the electrolytic estimation of molybdenum, the metal is separated in the form of the hydrated sesquioxide, and is then dried and converted into the trioxide by ignition at 425°; sublimation occurs at 450°. The separated sesquioxide or hydroxide has an electrolytic and at first a pseudo-metallic conductivity. On account of the poor yield, the electrolytic preparation of hydrated molybdenum sesquioxide is not practicable. Pure molybdenum, freezing point 2250°, D 8.95, prepared from the commercial metal, can be formed into sticks without pressure, treatment with a current of hydrogen for five to six hours at 2250°, however, being necessary for the reduction of included oxides. Pure molybdenum free from oxide is converted by chlorine into black, deliquescent molybdenum pentachloride, which on treatment with hydrogen at 250° yields the deep brownish-red, amorphous trichloride; this, when heated in a current of carbon dioxide, decomposes gradually with formation of the volatile tetrachloride and the refractory pale yellow, amorphous dichloride; the lower chlorides of molybdenum are much more stable than the higher towards air and water. In the preparation of the dichloride from molybdenum, it is important to exclude every trace of oxygen, because when heated in air the dichloride gives a cloudy white sublimate and a black residue of oxide. The dichloride gives yellow solutions in aqueous sodium hydroxide or potassium hydroxide, which deposit the black dihydroxide when boiled. The alcoholic solution conducts the electric current, the molecular conductivity increasing on dilution; hydrogen and

the oxychloride,  $\text{Mo}_2(\text{OH})_2\text{Cl}_4$ , and sometimes molybdenum, are liberated at the cathode, whilst acetaldehyde and ethyl chloride are formed at the anode. By combination with an alcoholic calomel electrode, the electrolytic potential for molybdenum/molybdenum dichloride dissolved in alcohol has a value 0.552 volt referred to the hydrogen electrode as zero. In the potential series molybdenum falls between mercurous mercury and trivalent antimony. The alteration of the potential with dilution corresponds only qualitatively with Nernst's formula.

D. F. T.

**Electric Nebulae of Antipyretica.** H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1272—1277).—The electric charge which is developed when a solution of an odorous substance in water is sprayed (Zwaardemaker, A., 1917, ii, 63; see also Backman, A., 1917, i, 498) is also produced by solutions of other substances, odorous or odourless, such as saponins, glucosides, alkaloids, antipyretica, and other physiologically active substances. In order to produce the electric phenomenon, the substance, added to water and sprayed with it, must satisfy certain conditions: (1) it must be soluble in water; (2) it must lower the surface tension; (3) it must volatilise when spread over a large evaporation area. Inorganic acids and salts, glycerol, sugars, dextrin, lecithin, and albumin do not produce the phenomenon.

A saturated aqueous solution of the antipyretic alkaloids, quinine, quinidine, cinchonine, cinchonidine, etc., sprayed under an over-pressure of 2 atmos., charges positively a screen at a distance of about 25 cm., the air around it and at some distance from it being charged negatively. The effect is less pronounced than that caused by odorous substances.

The charge produced by salicylic acid and its derivatives varies from zero in the case of insoluble phenyl and benzyl salicylates to a moderate effect with salts of salicylic acid and to effects caused by salicylic acid and its liquid derivatives, which are sometimes stronger than those due to typical odorous substances such as camphor. The salts owe their electrifying power to the anion; the cation lessens the charge of the nebula. The optimal electrifying power of salicylic acid is produced by a millinormal solution.

The third group of antipyretica examined comprises quinoline derivatives, pyrazoles, and *p*-aminophenols. The electric phenomenon is produced by pyramidone, phenacetin, and citrophen with moderate intensity, somewhat more strongly by kairine, and is extremely distinct in the case of antipyrine, salipyrine, acetopyrine, tussol, antifebrin, and euphorine.

To obtain normal results, the sprayer must be earthed. The magnitude of the electric charge is greatly affected by the addition of sucrose or sodium chloride to the solution. The charge is always increased by the former, but the effect of sodium chloride depends on its concentration.

C. S.

**New Cryoscopic Tube and Method.** GIUSEPPE ODDO (*Gazzetta*, 1917, 47, ii, 188—199).—The tube described and figured differs from the usual form in having a wide side-tube set obliquely to the main tube near the bottom of the latter. This tube is closed with a stopper, and is used for the rapid introduction of solvent and substance. The arrangement is intended more especially for working with very hygroscopic substances. R. V. S.

**Condition of Substances in Solution in Absolute Sulphuric Acid. VI.** G. ODDO and A. CASALINO (*Gazzetta*, 1917, 47, ii, 200—232. Compare Oddo and Scandola, A., 1910, ii, 1035).—Continuing this investigation, the authors have studied the behaviour of thirty-one organic acids dissolved in absolute sulphuric acid. In the case of the monocarboxylic acids, such as *n*-butyric acid, the molecular weight observed is a little more than 50% of the true molecular weight, indicating that these acids form dissociated oxonium salts. Among the dicarboxylic acids, oxalic acid gives the highest values, exceeding 80% of the molecular weight, and the percentages observed increase with the concentration. The rest of the acids examined in this series have apparent molecular weights which are smaller the more distant the two carboxyls, and the figures obtained decrease with the concentration. The conclusions which may be drawn from the experimental data as to the constitution of solvent and solutes are discussed. R. V. S.

**Condition of Substances in Solution in Absolute Sulphuric Acid. VII.** G. ODDO and A. CASALINO (*Gazzetta*, 1917, 47, ii, 232—243. Compare preceding abstract).—This paper deals with the behaviour of certain aldehydes, ketones, lactones, and anhydrides in absolute sulphuric acid. The aldehydes, ketones, and lactones behave like the monobasic acids described in the preceding paper. Acetic anhydride has 48.9—34.3% of its true molecular weight, succinic anhydride 89.1—68.4%, and phthalic anhydride 111.7—89.0%. The variations in each case correspond with varying concentrations. R. V. S.

**The Laws of the Vapour Pressures of Water and of other Vapours.** PIETRO ENRICO BRUNELLI (*Nuovo Cim.*, 1917, [vi] 14, ii, 55—68).—The formula  $\log p = 23.08647 - 4.5 \log T - 2980.46/T - 0.00278T + 0.000002825T^2$ , where  $p$  is the pressure in mm. of mercury and  $T$  is taken to be  $273.09 + t$ , gives the vapour pressure of water more exactly and over a longer range of temperature than any of those hitherto proposed. Similar formulae are given for carbon dioxide and ammonia, and in these cases also the agreement with observed values is satisfactory. R. V. S.

**The Saturated Vapour Pressures of Substances of High Atomicity.** E. ARIÈS (*Compt. rend.*, 1918, 167, 267—270. Compare this vol., ii, 294).—The formula given for compounds containing more than eight atoms in their molecule is  $\Pi = r^2/x$ , where

$x = \frac{1}{T}$ , and formulæ are given in the cases of pentane, hexane, heptane, and octane showing the variations of  $T$  with the reduced temperature  $r$ . The calculated values are in fairly close agreement with those observed by Young for these four hydrocarbons.

W. G.

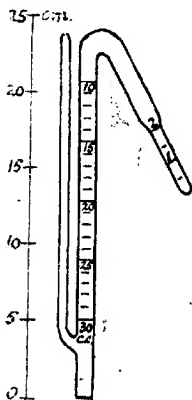
**The Manipulation of Volatile Substances. III.** ALFRED STOCK (*Ber.*, 1918, 51, 983—989. Compare A., 1917, ii, 442).—The following pieces of apparatus are described with diagrams, and an account is given of their applications.

I. An improved form of gas-holder for substances which can be condensed by liquid air (*ibid.*).

II. (a) An arrangement for filling a tube with a gas or mixture, without exposure to the air, and sealing it, for example, a mixture of hydrogen bromide, monosilane,  $\text{SiH}_4$ , and aluminium bromide, and (b) a simple device, "vacuum tube opener," for breaking the capillary of a sealed tube and leading off the gases it may contain without exposure to the air.

III. A simple apparatus for analysing gaseous mixture by measuring the pressure of the gas left uncondensed at different temperatures, suitable for cases in which the uncondensable impurity is not more than 25%, and is, of course, insoluble in the liquefied gas. The construction of the apparatus is sufficiently clear from the annexed diagram, and it is used as follows. A suitable volume of the gas is admitted into the measuring tube over mercury, which is easily done without disturbing the column in the side-limb, this serving as a manometer. The open end is closed with a good stopper, and the constricted end is then immersed in the cooling bath, such as liquid air, and when the levels of the mercury columns are steady, the volume of the unabsorbed gas is read off and the pressure upon it found from the difference in the mercury levels. The temperature of the residual gas will not be uniformly the same as the initial gas, for part of it will be within the range of the cooling-bath. A sufficiently accurate correction may be made by noting the contraction in volume when the tube is filled with air and the constricted end is placed in the bath, the immersion being to the same depth as in an actual analysis. Having now corrected the initial and final volumes to  $T.P.$ , the determination of the proportion of unabsorbed gas is simple.

J. C. W.



**Thermochemical Studies.** DANIEL LAGERLÖF (*J. pr. Chem.*, 1918, [ii], 97, 137—140).—As an extension of the earlier paper



(this vol., ii, 62), it is shown that if Zubow's experimental values are corrected by a divisor 1.00888 instead of 1.007, as suggested by Roth, the results thus obtained for *n*-hexane and *n*-octane are almost identical with those calculated by the author. D. F. T.

**The Characteristic Equation of Fluids.** PIERRE WEISS (*Compt. rend.*, 1918, 167, 293—296. Compare this vol., ii, 291).—A mathematical discussion of the subject. W. G.

**The Characteristic Equation of Fluids.** PIERRE WEISS (*Compt. rend.*, 1918, 167, 364—366. Compare preceding abstract).—By combining the equation expressing the law of dilatation (*loc. cit.*) and the general equation  $\Pi = a/v^n$  for the law of internal pressure, the characteristic equation of fluids becomes

$$(p + a/v^n)(v - b) = \zeta RT,$$

where *a*, *b*,  $\zeta$ , and  $\eta$  are constants, and *R* is the constant of perfect gases. Very different combinations of these constants may occur for the same substance, but generally the values  $\zeta = 1$  and  $\eta = 2$  in the region of large volumes, and in that of high densities  $\zeta$  is great and the co-volume is small. W. G.

**The Molecular Condition of Alloys in the Crystalline State and its Relation with the Form of the Equilibrium Diagram.** G. MASING (*Int. Zeitsch. Metallo.*, 1916, 9, 21—37, from *Chem. Zentr.*, 1918, i, 703—704).—The idea of extensive dissociation in compounds which over a considerable range of concentration are able to form mixed crystals with the two components is not opposed to crystallographic or general considerations; indeed, from the point of view of the phase rule also, dissociation is possible in the solid state with such compounds as opposed to compounds which are unable to form mixed crystals. A compound which is largely dissociated in the solid state and is capable of taking only small quantities of the components into solid solution can, as an independent crystalline entity, possess a slight solvent power for the components only over a small temperature interval in the immediate neighbourhood of the temperature boundary of its area of existence, for example, of the m. p. A highly dissociated compound which forms mixed crystals with its components over a wide range of temperature must also give rise to homogeneous mixed crystals over a large interval of concentration. If, however, the crystalline form of a compound possessing very limited miscibility is stable in the solid state over a wide range of temperature, the compound can be only slightly dissociated, and the extent of the possible dissociation is proportional to the breadth of the area of existence of the homogeneous crystals. It is thus possible from the equilibrium diagram to draw a conclusion as to the molecular condition of an alloy, but the decision concerns only the upper limit of the degree of dissociation; an extensive range of solubility in the solid state is not trustworthy evidence of extensive dissociation.

With compounds which are strongly dissociated in the solid state, the maximum in a fusion or transformation curve need not correspond with the composition of the compound, and the same limitation holds also for other properties, such as conductivity and its temperature-coefficients. The maximum (or minimum) under such conditions is only an indication of the existence of a compound. These deductions are not applicable to compounds which are stable over a wide range of temperature without taking the components into solid solution. There is no symmetrical relationship between solubility curves and the curves of homogeneous equilibrium.

D. F. T.

**The Artificial Coloration of Spherulites with Helicoidal Winding (Tartrates and Hydrogen Malates).** PAUL GAUBERT (*Compt. rend.*, 1918, 167, 368—370).—The spherulites are easily obtained, artificially coloured, if a solution of the substance containing some methylene-blue is evaporated as a thin layer on a glass plate. The temperature and velocity of crystallisation have a great influence on the production of these spherulites. The methylene-blue is in the crystalline state in the spherulites. Good results were obtained with ammonium hydrogen malate and the hydrogen tartrates of sodium, ammonium, rubidium, and thallium.

W. G.

**Chemical Studies on Physiology. V. "Soluble" and "Insoluble" Colloids, Genuine and Spurious Jellies, Protoplasma and Cell Permeability.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, 88, 232—282).—A theoretical paper. The authors distinguish between "soluble" and "insoluble" colloids. They assume that in all cases of solution the solute forms combinations with many molecules of the solvent, and solutions with all stages between molecularly dispersed and colloidal dispersed particles exist. The latter form "soluble" colloids. In contradistinction to these, "insoluble" colloids exist, which owe their dispersion to the adsorption of substances on their surface with great affinity for water. To the latter class proteins belong. The view of the authors on these substances has been expressed in previous papers. Gelatin is regarded as a mixture of polypeptides polymerised by means of calcium salts. Jellies are formed from colloids with great power of combining with water, and come into existence when the whole of the water in the system is accumulated on the surface of the colloidal particles. Corresponding with the "soluble" and "insoluble" colloids are the "genuine" and "spurious" jellies, the former of which only are reversible. The authors discuss the application of their ideas to the problems of cell permeability and metabolism.

S. B. S.

**Chemical Equilibria in the Reduction and Cementation of Iron.** RUDOLF SCHENCK (*Zeitsch. Elektrochem.*, 1918, 24, 243—255).—A general résumé of work on the iron-carbon, iron-carbon monoxide, and similar equilibria.

J. F. S.

**Propagation of Flame through Tubes of small Diameter.** WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1918, 113, 656—666).—In continuation of previous experiments on the speed of the "uniform movement" during the propagation of flame in mixtures of methane and air, observations have been made with tubes of small diameter. The results obtained show the increased cooling effect of the walls of the tube as its diameter is decreased, in that the apparent limits of inflammability are narrowed considerably. It is also found that the speeds of the flames tend towards a constant value of about 35 cm. per second as the limiting mixtures are approached, and it is supposed that this represents the slowest speed at which continued propagation of flame ("uniform movement") is possible in mixtures of methane and air.

Experiments made on the propagation of flame through tubes open at both ends, the mixture of methane and air in the tube being ignited near one end of the tube, show that the distance travelled before vibrations are set up which lead to the extinction of the flame depends on the length and diameter of the tube and on the composition of the mixture. The distance increases with the length and the diameter of the tube and diminishes as the percentage of methane in the mixture approaches that corresponding with the maximum speed of propagation of the flame (9.5—10% methane). In consequence of these relations, it follows that a length of tube the diameter of which is small enough to prevent the passage of flame in the mixture which corresponds with maximum speed of flame propagation may fail to do so when the mixture contains a smaller proportion of methane.

Further experiments described have reference to the propagation of flame through short lengths of narrow brass tubes from vessels filled with inflammable mixtures. The explosion vessels, consisting of tubes 2 cm. in diameter and of different lengths, contained 10% mixtures of methane and air. The mixture was ignited near the closed end, and the speed with which the flame reached the narrow brass exit tube was varied by varying the length of the explosion tube. The results obtained with brass tubes from 4 to 8 mm. in diameter, and with explosion vessels varying in length from 10 to 40 cm., show clearly that the increased speed of propagation of the flame reduces considerably the protection which is afforded by the narrow brass exit tubes.

H. M. D.

**Relative Activities of Methyl, Ethyl, and *n*-Propyl Iodides with Sodium  $\alpha$ - and  $\beta$ -Naphthoxides.** HENRY EDWARD COX (T., 1918, 113, 666—674).—The rate of the reactions between the alkyl iodides and sodium  $\alpha$ - and  $\beta$ -naphthoxide in ethyl-alcoholic solution has been measured at 40°. For equivalent quantities of the reacting substances, the course of the reaction is satisfactorily represented by the equation for a bimolecular change. The magnitude of the velocity-coefficient increases, however, with the dilution of the original solution. The coefficient  $k_v$  for dilution  $v$  can be expressed in the form  $k_v = k_1 + a \log v$ . This equation holds for

ethyl and *n*-propyl iodides at least as far as  $v=40$ . For methyl iodide, the relation holds up to  $v=10$  in the case of sodium  $\alpha$ -naphthoxide and to  $v=7$  for the  $\beta$ -naphthoxide. At higher dilutions, methyl iodide reacts more rapidly than would be expected from the empirical formula.

The reactivity of the iodides decreases with increase in the weight of the alkyl group. Sodium  $\alpha$ -naphthoxide is more reactive than the  $\beta$ -compound. H. M. D.

**The Law of Action of Sucrase: Hypothesis of an Intermediate Compound.** H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1918, 167, 338—341).—When the sucrose is in excess with respect to the sucrase, the weight  $x$  of sugar hydrolysed in a time  $t$  is proportional to the quantity of sucrase  $n$  and independent of the initial concentration  $a$  of the sucrose. The velocity of inversion, at first constant, diminishes until the excess of sucrose has disappeared, at which point the value of the quotient  $(dx/dt)/(a-x)$  remains constant. If, on the other hand, the sucrase is in excess with respect to the sucrose, the rate of inversion is proportional to  $a$  and independent of  $n$ , and the velocity of hydrolysis, constantly decreasing, is such that the quotient  $(dx/dt)/(a-x)$  remains constant throughout. These results are in accord with Brown's hypothesis as to the formation of a compound between the sugar and the enzyme (compare T., 1902, 81, 373). W. G.

**Influence of Foreign Substances on the Activity of Catalysts. V. Experiments with Palladium Hydrosol in the Presence of the Hydroxides of Iron, Copper, and Zinc.** C. PAAL and WILHELM HARTMANN (*Ber.*, 1918, 51, 894—906. Compare this vol., ii, 303).—Ferric hydroxide is peptised to a certain extent by sodium protalbinat, but the amount of iron taken up is lessened by the addition of sodium hydroxide. Freshly precipitated ferric hydroxide does not hinder the catalysis of mixtures of hydrogen and oxygen by palladium hydrosol, protected by sodium protalbinat, nor does it suffer reduction under such conditions.

Cupric hydroxide is taken up by sodium protalbinat to a fairly considerable extent, and free sodium hydroxide enhances the peptisation. More concentrated cupric hydroxide hydrosols than have hitherto been described can therefore be made (compare A., 1906, ii, 358). Freshly precipitated cupric hydroxide lowers the activity of palladium hydrosol towards hydrogen and oxygen mixtures, but large quantities would be necessary to spoil the catalyst entirely. With colloidal cupric hydroxide, however, the activity of the catalyst actually increases for a time, but then falls off rather rapidly. In both cases the falling off is not regular, for after some time a slight recovery sets in, followed again by further loss of activity.

Zinc hydroxide is also peptised by sodium protalbinat. This

depresses the activity of palladium hydrosol during the first hour of an experiment to about half the normal, but a remarkable recovery then sets in, and the catalyst actually becomes slightly more active than usual, although it still contains colloidal zinc hydroxide.

J. C. W.

**Inhibition of Foaming.** CYRUS H. FISKE (*J. Biol. Chem.*, 1918, 35, 411—413).—From a consideration of the manner of action of substances which inhibit foaming, the author draws the conclusion that the chief properties contributing to the efficiency of an organic liquid as a foam inhibitor are as follows: high surface activity, high surface tension, high interfacial tension, low solubility, and low volatility. A substance which possesses these characteristics is *isoamyl isovalerate* (or a mixture of this substance with *isoamyl alcohol*). To prepare the reagent, 28 c.c. of anhydrous *isovaleric acid*, 30 c.c. of *isoamyl alcohol*, and 1 c.c. of concentrated sulphuric acid are boiled together for one hour under a reflux condenser. The resulting ester is carefully freed from acid by shaking with sodium carbonate and then well washed with water. It may be used at once or after distillation. An alternative method of preparation is to oxidise *isoamyl alcohol* with potassium dichromate and sulphuric acid; the product contains some *isovaleraldehyde*, which can, however, be removed by shaking with sodium hydrogen sulphite solution.

H. W. B.

**A Simple Gas Generator.** BRUCK (*Chem.-techn. Woch.*, 1917, 1, 246; from *Chem. Zentr.*, 1918, i, 690).—A small generator working on the same principle as Kipp's apparatus is constructed from a wide glass tube by fitting it internally near its closed end with a perforated shelf of rubber or similar material. The neck of the tube is fitted with a cork; through this passes a test-tube to which has been sealed concentrically a narrow glass tube, this glass tube reaching through the shelf to the bottom of the wide containing tube. For the generation of hydrogen, zinc is placed on the shelf and hydrochloric acid introduced at the mouth of the test-tube; the acid flows through the test-tube and its extension into the end of the wider tube, and then rises until it passes through the shelf to the zinc.

D. F. T.

**Aspirator.** J. M. JOHLIN (*J. Ind. Eng. Chem.*, 1918, 10, 632).—A large glass bottle, serving as the reservoir, is closed by a cork carrying three tubes; one of these is the inlet or outlet for the gas, another is used as a siphon for emptying the water from the bottle when this is full, whilst water is admitted through the third tube so that the gas may be forced out. The water enters through a narrow jet in a wide tube fitted at the top of the third tube, the wide tube being provided with a side-tube which carries off any excess of water.

W. P. S.

**Safety Valve.** E. RITTENHOUSE (*J. Ind. Eng. Chem.*, 1918, 10, 633).—A short length of glass tube has a small bulb at its lower

end and a narrow central tube is sealed to the inner wall and extends almost to the bottom of the bulb; a globule of mercury in the bulb seals the lower end of the central tube. When this piece of apparatus is inserted in a hole in a cork closing a flask, air may enter through the central tube, bubble through the mercury, and enter the flask through a small opening in the wall of the tube above the bulb. The valve is useful when ammonia is being distilled and absorbed in standard acid; air is admitted to the flask during any temporary decrease in pressure in the latter, thus preventing the standard acid from being drawn into the flask. Vapours cannot escape through the valve outwards owing to the mercury rising in the central tube.

W. P. S.

**Filtration Apparatus.** F. HÄRTEL (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 444—445).—An apparatus for filtration under reduced pressure consists of a rectangular specimen jar without a neck and having a square, overlapping lid. The jar is laid on its side, and in the upper side are bored two holes, one for receiving the stem of a funnel or filter tube and the other a tube provided with a three-way tap and connected with a pump. The vessel (beaker, flask, etc.) in which the filtrate collects is placed in the jar beneath the stem of the funnel. The apparatus enables the filtrate to be collected directly in a vessel, in which it may be subjected to any further treatment, and transference from a filter-flask is avoided.

W. P. S.

**Ultra-filtration of Small Quantities of Liquid by Centrifugal Force.** D. J. DE WAARD (*Arch. Néerland. Physiol.*, 1918, **2**, 530—533).—The apparatus consists of a thick glass tube about 30 cm. long and 1 cm. bore separated from a similar tube, closed at its distal end, by a nickel disk pierced with openings about 2 mm. in diameter. The membrane is placed on the disk, and then the tubes are pressed firmly on to the disk by means of a screw cap and collars attached to the tubes. The whole apparatus now resembles a test-tube divided into an upper and a lower portion by the disk supporting the membrane. A minute hole is pierced in the side of the lower tube just below the collar to allow of the escape of air. The liquid to be filtered is poured on the membrane, and the apparatus then placed in a centrifugal machine. If the number of revolutions per minute is about 3000, the filtration pressure is about 6 atmospheres per sq. cm. The membrane may be of animal origin, or prepared from celloidine or other material by Walpole's method. During centrifugalisation, the lower tube should be protected by an outer tube of copper, the intervening space being filled with oil.

• H. W. B.

**New Form of Ultra-filter. Some of its Uses in Biological and Synthetic Organic Chemistry.** PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1918, **40**, 1226—1230).—Quantitative dialysis has hitherto been impossible on account of the extreme

dilution of both filtrate and residue caused by the dialysing water. Through the discovery that all semipermeable membranes pervaporate (Kober, A., 1917, ii, 295), the difficulties of ultra-filtration by dialysis have been completely overcome. An apparatus, consisting essentially of a dialyser with automatic water supply connected by a siphon to a pervaporator, is figured and described. Its action depends on pervaporating both the dialysate and the diffusate solutions during dialysis, whereby quantitative dialysis is rendered possible.

The author gives a few examples showing that in biological or synthetic work humus material or highly coloured by-products, which cannot be removed by charcoal, are rapidly or completely removed by ultra-filtration. [See also *J. Soc. Chem. Ind.*, October.]  
C. S.

**Device to ensure Tight Connections between Glass and Rubber Tubing.** C. C. KIPLINGER (*J. Ind. Eng. Chem.*, 1918, 10, 631).—A piece of stout string is tied round the joint and is tightened by slipping a piece of metal wire between the string and rubber, and twisting the wire until the string is quite tight; the ends of the wire are then bent round the tube.  
W. P. S.

## Inorganic Chemistry.

**Enrichment of Iodine during its Purification.** FRANCESCO LENCI (*Boll. chim. farm.*, 1918, 57, 121—123).—In the purification of iodine, sublimation removes most of the cyanogen iodide, which sublimes first, and also the bromine and moisture, and sublimation in presence of potassium iodide gets rid of chlorine and bromine. Loss of iodine during the purification may be avoided by treatment based on the results obtained by Tarugi (this vol., ii, 203). [See, further, *J. Soc. Chem. Ind.*, 579A.]  
T. H. P.

**The Theory of Transmission of Oxygen.** ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1918, [vii], 18, 17—18).—Certain metallic salts, particularly copper salts, behave as anaeroxydases, and the authors conclude that these substances have secondary valencies having the power to take up oxygen and to transmit it at once under suitable conditions. Anaeroxydases and copper salts behave alike in the oxidation of guaiacum resin in the presence of hydrogen peroxide.  
W. P. S.

**Reduction of Sulphuric Acid by Carbon Monoxide.** JAN. MILBAUER (*Chem. Zeit.*, 1918, 42, 313—315).—At 250°, sulphuric acid is reduced by carbon monoxide according to the equation

$\text{H}_2\text{SO}_4 + \text{CO} = \text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O}$ ; about 25 mg. of sulphur dioxide are produced per hour when carbon monoxide is passed at the rate of 0.6 litre per hour through a layer of sulphuric acid 9.5 cm. in height. The reaction proceeds as long as the strength of the sulphuric acid does not fall below 91%, and is accelerated by the presence of certain catalysts, such as palladium, iridium, mercury, selenium, silver, gold, tin, etc. Platinum, osmium, and copper sulphate do not affect the rate of the reaction. W. P. S.

#### Preparation and Testing of Pure Arsenious Oxide.

ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1918, 10, 522—524).—Ordinary arsenious oxide is boiled for about one hour with a quantity of water insufficient to dissolve the whole of it, the solution filtered while hot, the filtrate concentrated until arsenious oxide begins to precipitate, and the solution again filtered. The separated oxide is tested for antimony by dissolving a portion in ammonia, adding hydrogen sulphide, boiling the mixture, and then cooling in ice-water; a turbidity is obtained if more than 0.15% of antimony trioxide is present, and in such case the arsenious oxide must be treated further as described. The purification depends on the fact that antimony, if present, is absorbed almost completely by the solid arsenious oxide which remains undissolved in the aqueous solution. The final crystallisation of the pure arsenious oxide is best made from a slightly hydrochloric acid solution, and the product is then sublimed. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

#### Silicon Hydrides. V. Decomposition of Silicon Hydrides by Water. Action of Hydrogen Bromide on Monosilane.

ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1918, 51, 989—996. Compare A., 1916, ii, 319; this vol., ii, 110, 111).—In the first communication on the silanes, it was reported that they suffer decomposition into silicic acid and hydrogen when left for a few hours in contact with water. It is now found that this reaction is largely conditioned by the alkalinity of the glass apparatus, for in quartz vessels, or with slightly acidified water practically no change takes place during several days.

This stability of the hydrides may be made use of in analysing mixtures of the three gases, monosilane, hydrogen bromide, and bromomonosilane. The last-named gas reacts immediately with water to form the gas disiloxane and hydrobromic acid, thus:  $2\text{SiH}_3\text{Br} + \text{H}_2\text{O} = (\text{SiH}_2)_2\text{O} + 2\text{HBr}$ . After two or three hours, the new gas reacts further to give hydrogen, thus:  $(\text{SiH}_3)_2\text{O} + \text{H}_2\text{O} = \text{SiO}_2 + 3\text{H}_2$ . If the volume of the mixture is  $a$  c.c., the volume after the initial contraction is  $b$  c.c., and the final volume after the production of hydrogen is  $c$  c.c., then  $c - b$  gives the volume of  $\text{SiH}_3\text{Br}$  and  $a - b - \frac{1}{2}(c - b)$  the volume of  $\text{HBr}$ .

From the point of view of carbon chemistry, a remarkable reaction of the silicon hydrides has now been discovered. Monosilane, for example, reacts very readily with hydrogen bromide in the



presence of aluminium bromide, according to the equation,  $\text{SiH}_4 + \text{HBr} = \text{SiH}_3\text{Br} + \text{H}_2$ ,  $\text{SiH}_4 + 2\text{HBr} = \text{SiH}_2\text{Br}_2 + 2\text{H}_2$ , etc. In one experiment, which is fully described, 207 c.c. of monosilane and 188.8 c.c. of hydrogen bromide were heated for three hours at  $100^\circ$  in a sealed tube of 700 c.c. capacity, on the walls of which a little aluminium bromide had been deposited by sublimation, when 86.7 c.c. of monosilane, 52.5 c.c. of  $\text{SiH}_3\text{Br}$ , and 67.8 c.c. of  $\text{SiH}_2\text{Br}_2$  were obtained from the product, practically all the hydrogen bromide having disappeared. This method is consequently better than direct bromination for the preparation of the lower bromides.

The apparatus employed is described in another paper (see this vol., ii, 353).  
J. C. W.

**Melting Points of Cristobalite and Tridymite.** J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1918, [iv], 46, 417—426).—Cristobalite prepared by heating clear quartz crystals for 144 hours at  $1300\text{--}1400^\circ$  melts at  $1710^\circ \pm 10^\circ$ .

Tridymite grains selected from the cristobalite mass were converted into cristobalite at  $1667\text{--}1677^\circ$  without melting. Two specimens of natural tridymite (one from Nevada and one from Mexico) both melted sharply at  $1670^\circ \pm 10^\circ$ . The results confirm those of Fenner (A., 1913, ii, 133), showing that the region of stability of cristobalite is above that of tridymite. [See, further, *J. Soc. Chem. Ind.*, 546A.]  
A. B. S.

**A Supposed Fusion of Carbon by O. Lummer.** M. LA ROSA (*Gazzetta*, 1917, 47, ii, 19—31).—The author criticises Lummer's conclusions (*Verflüssigung der Kohle*, etc., Braunschweig, July, 1914), and directs attention to some of his earlier experiments.  
T. H. P.

**Residual and Extinctive Atmospheres of Flames.** THOMAS FRED ERIC RHEAD (*J. Soc. Chem. Ind.*, 1918; 37, 274—278r).—Experiments have been made with the flames of a number of different gases to determine the amount of oxygen in (1) the "residual atmosphere," that is, the atmosphere in which the flame, burning in a limited supply of air, becomes extinguished, and (2) the "extinctive atmosphere," that is, the mixture of oxygen and nitrogen which is just unable to support combustion of the gas.

The residual atmospheres of flames of the hydrocarbons methane, propane, butane, and pentane were found to contain from 15.6% to 16.4% of oxygen, the value increasing gradually with the molecular weight. For cyanogen, the value found was 15.3%, for carbon monoxide 10.2%, and for hydrogen 5.7%. The oxygen content of the residual or extinctive atmosphere depends primarily on the rate of diffusion of the combustible gas into the atmosphere and on the complexity of the combustion process. Hydrogen, with a high rate of diffusion, a simple reaction, and a high initial rate of flame propagation in air, therefore leaves an atmosphere with a low oxygen content.

For the examination of the extinctive atmospheres, a novel experimental method was devised, consisting in feeding a flame with a mixture of air and nitrogen which could be varied at will with considerable nicety. The mixture which just extinguished the flame was taken as the extinctive atmosphere. The oxygen content in the case of the hydrocarbons methane to pentane was found to be practically constant at 16.3–16.6%, with a constant speed of the gas stream and of the current of air–nitrogen mixture. It was found, however, that the flame would continue to burn in an atmosphere containing less oxygen when the atmosphere was supplied at a greater speed. Coal gas behaves differently from a pure gas, on account of the widely different extinctive atmospheres of its two principal constituents, hydrogen and methane. Experiments on a mixture of these gases showed that in the presence of an atmosphere of low oxygen content the hydrogen burns preferentially. The methane under these conditions acts mainly as a diluent, and this accounts for the observation that in the case of coal gas the oxygen content of the extinctive atmosphere is diminished by increasing the speed of the gas stream.

E. H. R.

**The Ternary System—Sodium Sulphate, Ammonium Sulphate, and Water. The Utilisation of Nitre Cake for the Production of Ammonium Sulphate.** HARRY MEDFORTH DAWSON (T., 1918, 113, 675–688).—An account is given of the equilibrium relations in the system  $\text{Na}_2\text{SO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$  at temperatures between  $-20^\circ$  and  $100^\circ$ . The characteristic features of the system, which are illustrated by diagrams of a somewhat novel type, are largely determined by the formation of the ternary compound  $\text{Na}_2\text{SO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ , which may exist in contact with solutions at any temperature between  $-16^\circ$  and  $59.3^\circ$ . Below  $-16^\circ$ , the double salt, in contact with solution, is decomposed, with the formation of Glauber's salt and ammonium sulphate, and above  $59.3^\circ$  it decomposes with the formation of the anhydrous simple salts. Other invariant temperatures are  $-19.5^\circ$ , at which Glauber's salt, ammonium sulphate, and ice co-exist in equilibrium with saturated solution, and  $26.5^\circ$ , at which the saturated solution is in equilibrium with Glauber's salt, anhydrous sodium sulphate, and the double salt.

The curves which show the influence of temperature on the composition of the solutions saturated with respect to two solid phases are distinguished by the fact that the solutions saturated with respect to Glauber's salt and the double salt show a rapid diminution in the ammonium sulphate concentration and a rapid increase in the sodium sulphate concentration as the temperature rises from  $-16^\circ$  to  $26.5^\circ$ . On the other hand, solutions saturated with respect to anhydrous sodium sulphate and the double salt show a decrease in the sodium sulphate concentration and a remarkably rapid increase in the ammonium sulphate concentration as the temperature rises from  $26.5^\circ$  to  $59.3^\circ$ .

Between  $-16^\circ$  and  $20^\circ$ , the double salt is decomposed by water

with the separation of Glauber's salt, and between  $41.5^{\circ}$  and  $59.3^{\circ}$  it is similarly decomposed with the separation of anhydrous sodium sulphate. These intervals of temperature represent the lower and upper transition intervals.

In virtue of the considerable differences in the values of the ratio of ammonium sulphate to sodium sulphate in the saturated solutions at high and low temperatures, it is possible to separate these salts by crystallisation under suitably controlled conditions. A method has been devised in which solutions of appropriate concentration are cooled to a temperature of about  $-10^{\circ}$ , when Glauber's salt separates out, the mother liquors being subsequently evaporated at about  $100^{\circ}$  when pure ammonium sulphate is deposited until the ratio of ammonium sulphate to sodium sulphate in the hot solution has fallen to a value much smaller than that characteristic of the mother liquor from the crystallisation process.

H. M. D.

**Composition of Lime-Sulphur Solutions.** O. B. WINTER (*J. Ind. Eng. Chem.*, 1918, 10, 539—545).—Lime-sulphur solution which has been prepared from ordinary commercial lime and sulphur, and has been kept for several days, does not contain any appreciable amount of hydrogen sulphide, calcium hydrosulphide, calcium hydroxyhydrosulphide, or the corresponding salts of other metals; free calcium hydroxide is not present. When, however, an excess of lime has been used in preparing the lime-sulphur solution, or when the latter has been diluted with lime-water, free calcium hydroxide may be present for a time, but gradually disappears. The addition of magnesium sulphate to lime-sulphur solution produces a slight increase in the monosulphide sulphur and sulphide sulphur contents, whilst the thiosulphate sulphur content is not affected; the magnesium replaces calcium, magnesium polysulphide being formed and calcium sulphate crystallising from the solution. Free sulphur does not appear to be present in lime-sulphur solution, and any sulphur which separates is derived from the higher polysulphides. The orange-red crystals which separate from concentrated lime-sulphur solution have the composition  $2\text{CaO} \cdot \text{CaS}_8 \cdot 11\text{H}_2\text{O}$ , but it is improbable that they exist in this form in the solution. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**Influence of the Temperature of Burning on the Rate of Hydration of Magnesium Oxide.** EDWARD DE MILLE CAMPBELL (*J. Ind. Eng. Chem.*, 1918, 10, 595—596).—When magnesite is ignited at or below  $1100^{\circ}$ , the resulting magnesium oxide, when immersed in water, is hydrated completely within three months; if the ignition is made at  $1450^{\circ}$ , only 70% of the magnesium oxide is hydrated in six years. These results show that materials containing free magnesium oxide, if ignited at temperatures approaching that used in the production of Portland cement, will not be hydrated completely, even when immersed continuously in

water, until after the lapse of twenty years or more. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Ternary Systems Lead-Bismuth-Silver and Lead-Gold-Silver.** MASAHARU GOTO (*J. Coll. Eng. Tokyo*, 1918, 9, 63—114).—In the system lead-gold-silver, no ternary eutectic occurs. The temperature of the eutectic falls continuously from 350° for the lead-silver alloys to 208° for the lead-gold ones. The presence of gold reduces the power of silver of holding lead in solid solution. No compound is present. In the lead-bismuth-silver system, a ternary eutectic occurs containing 0.2% Ag, 43.6% Pb, and 56.2% Bi, which melts at 120°. Solid solutions occur in a narrow area around the silver corner of the diagram. F. C. TH.

**Compounds of Lead Fluoride and Chloride with Lead Phosphate.** M. AMADORI (*Atti R. Accad. Lincei*, 1918, [v], 27, i, 143—148).—The results obtained in the thermal study of the system lead fluoride-lead phosphate (A., 1913, ii, 216) were vitiated, owing to the presence in the phosphate both of a slight excess of lead oxide and apparently also of traces of another substance the nature of which was not determined. The examination of this system has now been repeated, the lead phosphate used being prepared from the calculated quantities of lead oxide and pyrophosphate, the latter itself being obtained by precipitation of lead nitrate with disodium hydrogen phosphate. The results show that fused mixtures of lead orthophosphate and fluoride form, on solidification, the compound  $\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbF}_2$ , which solidifies at 1093°. This compound and the analogous chloropyromorphite,  $\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2$ , solidifying at 1156°, correspond in composition with the mineral pyromorphite and undergo no transformation during cooling. Each of these compounds exhibits little if any miscibility with its components. T. H. P.

**Action of Hydrogen Sulphide on Mercuric Bromide.** GIAMBATTISTA FRANCESCHI (*Boll. chim. farm.*, 1918, 47, 221—223).—The addition of a few drops of an alcoholic solution of hydrogen sulphide to an alcoholic solution of mercuric bromide produces slight milkiness, mercurous bromide and sulphur being formed:  $\text{H}_2\text{S} + 2\text{HgBr}_2 = \text{Hg}_2\text{Br}_2 + \text{S} + 2\text{HBr}$ . Addition of a greater proportion, but not an excess, of the hydrogen sulphide solution causes the precipitation of the canary-yellow double salt,  $2\text{HgS} \cdot \text{HgBr}_2$  ( $?\text{Hg}[\text{S} \cdot \text{HgBr}_2]$ ).

whilst when excess is added, black mercuric sulphide is precipitated. The successive reactions are represented by the equations: (1)  $\text{H}_2\text{S} + 2\text{HgBr}_2 = \text{Hg}_2\text{Br}_2 + \text{S} + 2\text{HBr}$ ; (2)  $\text{H}_2\text{S} + 3\text{Hg}_2\text{Br}_2 + 3\text{S} = 2(2\text{HgS} \cdot \text{HgBr}_2) + 2\text{HBr}$ ; (3)  $\text{H}_2\text{S} + \text{HgS} \cdot \text{HgBr}_2 = 2\text{HgS} + 2\text{HBr}$ .

T. H. P.

**Recovery of Molybdic Acid.** W. H. LYNAS (*Met. and Chem. Eng.*, 1918, 169).—The following method is suggested for recover-

ing molybdic acid from the filtrates from phosphorus estimations. To the boiling filtrates from 3500 c.c. of ammonium molybdate solution, 200 grams of commercial sodium phosphate are added. The precipitate is washed by decantation and dried on a sand-bath; it is then dissolved in ammonia and the phosphorus precipitated by the addition of magnesium nitrate solution and filtered. The volume of the filtrate is made up to 3500 c.c. by the addition of 1900 c.c. of 1:1 nitric acid. [See, further, *J. Soc. Chem. Ind.*, October.] F. C. TR.

**Bismuth Tellurides. II.** M. AMADORI (*Atti R. Accad. Lincei*, 1918, [v], 27, i, 131—134. Compare A., 1915, ii, 783).—The author has subjected to thermal investigation that part of the Bi-S-Te system comprising the compositions of other natural sulpho-tellurides, that is, Bi-Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>S<sub>3</sub>. It is found that the single components, Bi, Bi<sub>2</sub>S<sub>3</sub>, and Bi<sub>2</sub>Te<sub>3</sub>, and the compound, Bi<sub>2</sub>S<sub>3</sub>.Bi<sub>2</sub>Te<sub>3</sub>, separate out from fused mixtures either in the pure state or in simple eutectic mixtures; there is no formation of new compounds and no miscibility relationships between these substances. No phenomena are observed which are attributable to the formation of substances analogous to tetradimite, grunlingite, or joseite. T. H. P.

## Mineralogical Chemistry.

**Anhydrite in the Boulders carried by the Lava of Stromboli.** G. PONTE (*Atti R. Accad. Lincei*, 1917, [v], 26, ii, 348—350).—The mineral has the percentage composition:

CaO.	SO <sub>2</sub> .	BaO.	SrO.	SiO <sub>2</sub> .	FeO <sub>2</sub> .
42.09	57.79	0.04	0.06	traces	0.02

R. V. S.

## Analytical Chemistry.

**Calculation of Analytical Results.** J. GROSSFELD (*Chem. Zeit.*, 1918, 42, 389—391).—Tables are given showing the equivalents and analytical factors of a large number of elements, inorganic compounds, organic compounds, and acids, sugars, alkaloids, etc. W. P. S.

**Graphic Methods of Analysis.** HANS GRADENWITZ (*Chem. Zeit.*, 1918, **42**, 368).—The system of curves suggested previously by the author (this vol., ii, 245) merely indicates the application of this method of analysis; no claim is made for priority or for the particular trustworthiness of the diagrams given.  
W. P. S.

**Graphic Methods of Analysis.** WA. OSTWALD (*Chem. Zeit.*, 1918, **42**, 367—368).—The author recommends the use of Gibb's triangular scheme for plotting the curves employed in the estimation of the composition of ternary mixtures; this system is simpler and more trustworthy than that described by Gradenwitz (this vol., ii, 245, and preceding abstract).  
W. P. S.

**Use of the Dipping Refractometer.** WYATT W. RANDALL (*J. Ind. Eng. Chem.*, 1918, **10**, 629—630).—In using the immersion refractometer, the author has found that the temperature of the liquid under examination rises slightly when the metal cup containing the liquid is attached to the instrument, probably due to the conduction of heat from the air to the cup through the metal parts of the instrument. Untrustworthy readings are therefore obtained. This heating does not take place when small beakers are used in place of the metal cups.  
W. P. S.

**New Form of Colorimeter.** JOSEPH C. BOCK and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **35**, 227—230).—The new colorimeter differs from the Duboscq instrument in having only one plunger, the light from a mirror being thrown partly through the glass containing the liquid the colour intensity of which it is required to measure, and partly through a cell containing a known depth of liquid of standard colour.  
H. W. B.

**Use of the Interferometer in Gas Analysis.** F. M. SEIBERT and W. C. HARPSTER (*U.S. Bureau of Mines, Tech. Paper*, No. 185, 1918, 18 pp.).—A description of the application of the Rayleigh interferometer to gas analysis, especially in special work necessitating frequent analyses. Using a gas chamber 1 metre long, the precision is equivalent to the ordinary volumetric gas analysis made over mercury.

The accuracy of the measurements depends largely on the length of the gas chambers, and the refractive index must be measured with great precision for accurate work. The percentage error made in determining one component of a mixture depends also on the choice of a comparative gas, and it is found better to calibrate the instrument empirically against some exact analytical method.

In order to obtain an accuracy of 0.02%, when using as a gas of comparison the gas that predominates in the mixture, the absolute refraction coefficients should differ by about 0.0001; therefore the greater the difference of the coefficients of absolute refraction, the

greater is the accuracy of the method. The gases compared must be dry and at the same temperature. [See, further, *J. Soc. Chem. Ind.*, 608a.] C. A. K.

**Electrical Conductivity Recorder for Salinity Measurements.** E. E. WEIBEL and A. L. THURAS (*J. Ind. Eng. Chem.*, 1918, 10, 626—627).—The apparatus described gives a continuous record of the salinity or density of a solution by the measurement of its electrical conductivity; it may be used for the concentration of brines and other salt solutions, and also many other substances the composition of which is constant during changes in concentration. Two electrolytic cells are used and are connected with a suitable alternating current galvanometer and a recorder. Temperature compensation is effected by placing both cells, which are in the two arms of a Wheatstone bridge, in a uniform temperature-bath or directly in the solution under examination.

W. P. S.

**A New Physico-chemical Volumetric Method.** REX DUBRISAY (*Ann. Chim.*, 1918, [ix], 9, 25—48).—The method described for determining the acidity of a solution is based on the observation and measurement of the tension at the surface of separation of two non-miscible liquids. A definite volume of vaselin oil mixed with 2% of oleic acid is allowed to flow slowly into a known volume of the liquid under examination from a jet just plunged into it, and the number of drops formed is counted. This is repeated after the addition of known volumes of standard alkali, and it is found that there is a sudden rise in the number of drops formed at the point of neutralisation. The vaselin oil may be replaced by a solution of stearic acid in benzene. W. G.

**Decanting.** H. TILLISCH (*J. Ind. Eng. Chem.*, 1918, 10, 631).—The time required for a precipitate to settle is shortened considerably if the test-tube is inclined at an angle of 45°. W. P. S.

**Neutralisation of Hydrogen Peroxide by Sodium Borate.** J. CAMBE and H. DIACONO (*J. Pharm. Chim.*, 1918, [vii], 18, 12—17).—The presence of small quantities of hydrofluosilicic acid or hydrofluoric acid in hydrogen peroxide inhibits the formation of a red coloration when the peroxide is treated with phenolphthalein and an excess of sodium borate; freshly prepared hydrogen peroxide, which contains "active oxygen," also fails to give a red coloration when treated with an excess of sodium borate in the presence of phenolphthalein. Other indicators are not affected by the above-mentioned substances. W. P. S.

**Estimation of Chlorine in Presence of Silicates.** G. BRUNNS (*Zeitsch. angew. Chem.*, 1918, 31, [i], 156).—In estimating chlorine in mixtures containing silicic acid, it is unnecessary

to render the silica insoluble and separate it by filtration. Mohr's method of titrating the chlorine with silver nitrate is trustworthy provided that the liquid be made neutral to phenolphthalein by means of nitric acid, and any gelatinous silicic acid be finely distributed throughout the liquid. C. A. M.

**Source of Error in Bunsen's Method for the Estimation of Peroxides, Chlorates, etc.** E. RUPP (*Zeitsch. anal. Chem.*, 1918, **57**, 226—230).—When manganese dioxide, potassium chlorate, etc., are estimated by distilling the substance with hydrochloric acid, collecting the distillate in potassium iodide solution, and titrating the liberated iodine, the results obtained are from 0.5% to 2% too low. The error varies with the conditions of the distillation, and is due to reaction between chlorine and water vapour, hydrochloric acid and oxygen being formed. Fairly trustworthy results are, however, obtained if potassium iodide is added to the distillation mixture and the iodine then distilled, collected, and titrated. In some cases, where the hydrochloric acid is too concentrated, iodine in small amount is liberated from the potassium iodide by the action of the acid. W. P. S.

**Estimation of Sulphuric Acid and Barium as Barium Sulphate.** Z. KARAOGLANOW (*Zeitsch. angew. Chem.*, 1918, **31**, 160).—A criticism of an investigation recorded by Winkler (*Zeitsch. angew. Chem.*, 1917, **30**, 301—303) on the gravimetric estimation of sulphuric acid and barium. The author has shown recently (this vol., ii, 47) that potassium salts influence the results, and that the presence and concentration of the hydrochloric acid, the time of precipitation, temperature, all have an effect on the precipitation of the barium sulphate. There is no evidence that barium hydrogen sulphate is formed during the precipitation.

W. P. S.

**The Microchemical Estimation of Nitrogen.** IVAR BANG (*Biochem. Zeitsch.*, 1918, **88**, 416—419).—A reply to some criticisms of Schollema and Hitterschy (*ibid.*, 1917, **84**, 354, 371). S. B. S.

**Use of Sodium Sulphate in the Kjeldahl-Gunning Method.** T. DOWELL and W. G. FRIEDEMAN (*J. Ind. Eng. Chem.*, 1918, **10**, 599—600).—The authors find that sodium sulphate (either anhydrous or an equivalent quantity of the crystallised salt) is as effective as is potassium sulphate in the digestion part of the Kjeldahl-Gunning method. W. P. S.

**Estimation of Ammonia in Urine.** A. LÉCLÈRE (*Compt. rend. soc. biol.*, 1917, **80**, 959—962; from *Physiol. Abstr.*, 1918, **2**, 262).—By distilling urine with lithium carbonate, ammonia is rapidly and quantitatively liberated. The hydrolysing action on



urea and amino-acids is slight, so that only a small correction is necessary. S. B. S.

**Ammonia and Nitric Nitrogen Estimations in Soil Extracts and Physiological Solutions.** B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1918, 10, 600—605).—Ammonia nitrogen is estimated by the aeration method at the ordinary temperature in the presence of magnesium oxide or sodium carbonate; the ammonia is absorbed in acid towers, and the contents of the latter are distilled subsequently with magnesium oxide in the usual way. The residual liquid in the aeration flask is then acidified with sulphuric acid, heated, cupric hydroxide added, the mixture filtered, the filtrate boiled for thirty minutes with the addition of sodium hydroxide, and the nitrate reduced with Devarda's alloy, the resulting ammonia being estimated by distillation. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Estimation of Nitrites.** F. DIENERT (*Compt. rend.*, 1918, 167, 366—367).—The method is based on the reaction  $\text{NaNO}_2 + 2\text{HI} = \text{NaI} + \text{I} + \text{NO} + \text{H}_2\text{O}$ . Three flasks, (1) containing 50 c.c. of 4% potassium iodide, (2) containing 10 c.c. of *N*-sulphuric acid, (3) containing the solution of the nitrite, are connected in the order mentioned, and carbon dioxide passed through them until all air is displaced. The contents of (1) are then driven over into (2), and this mixture in turn into (3). Ten c.c. of a 20% solution of ammonium carbonate are then added, and the free iodine titrated by means of *N*/70-arsenious acid, of which 1 c.c. = 0.2 mg. of nitrous nitrogen. Care must be taken to avoid the entrance of oxygen into flask (3) until the liquid has been made alkaline by the addition of the ammonium carbonate. W. G.

**Colorimetric Estimation of Phosphoric Acid in Potable Water.** P. N. VAN ECK (*Pharm. Weekblad*, 1918, 55, 1037—1040).—The hydrazine sulphate employed in Riegler's colorimetric method for estimating phosphoric acid can be replaced by stannous chloride, the same blue coloration being produced. A. J. W.

**Estimation of Zeolitic Silicic Acid in Soils.** K. K. GEDROITZ (*Reprint*, pp. 400—406).—The method commonly used in Russian laboratories for the estimation in soils of so-called zeolitic silicic acid, that is, silicic acid liberated when the soil is treated with concentrated hydrochloric acid in the hot, is tedious and the author now describes a new method, which is rapid and does not necessitate the use of large platinum dishes. The results obtained by this method approximate closely to those given by the old method. T. H. P.

**Pressure Method for the Estimation of Carbon Dioxide in Carbonates.** W. H. CHAPIN (*J. Ind. Eng. Chem.*, 1918, 10, 527—529).—The carbonate is dissolved in dilute hydrochloric acid contained in a flask of known capacity; the flask is provided with

a small mercury manometer, and the weight and percentage of the carbon dioxide are calculated from the change in pressure. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Bisulphate Method of Estimating Radium.** HOWARD H. BAKER (*J. Ind. Eng. Chem.*, 1918, 10, 525—527).—In this method, the mineral is fused and boiled with a mixture of sodium and potassium hydrogen sulphates, and the emanation is passed into the ionisation chamber of an electroscope. Readings of the rate of discharge are made three hours after the introduction of the gas. When the mineral under examination contains thorium, the gas cannot be transferred directly to the electroscope during fusion, but must be collected in a gas burette to allow the thorium emanation to decay. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**Methods of Estimating Potassium.** A. VURTHEIM (*Chem. Weekblad*, 1918, 15, 827—842).—A critical survey of the literature of the estimation of potassium. A. J. W.

**Estimation of Zinc in Zinc Dust.** L. A. WILSON (*Eng. and Min. J.*, 1918, 106, 334—336).—A sample of zinc dust with ferric sulphate and a piece of platinum foil are placed in a small conical flask connected through a three-way tap with a measuring tube. The whole system is then filled with liquid saturated with hydrogen at the temperature of experiment, the flask and connecting tube containing water and the measuring tube 10% sulphuric acid. The addition of sulphuric acid through a separating funnel causes evolution of hydrogen, and if any fine particles of zinc are carried over, solution is completed by the acid in the measuring tube. Finally, water is run through the separating funnel to force the hydrogen into the measuring tube, and, after swelling, the volume is read off and corrected. C. A. K.

**Microchemical Reaction for Manganese.** J. B. MENKE (*Chem. Weekblad*, 1918, 15, 868—869).—A drop of ammonia containing cyanuric acid gives with manganese sulphate a precipitate of manganous hydroxide. After a few minutes, or immediately on boiling, colourless, unstable needles of high polarising power separate from the mixture. A. J. W.

**Rapid Method for the Estimation of Iron in small quantities of Blood.** LOUIS BERMAN (*J. Biol. Chem.*, 1918, 35, 31—236).—The iron held in combination in the blood is liberated by the action of concentrated hydrobromic acid, whilst the organic matter is destroyed by potassium permanganate and the iron simultaneously oxidised to the ferric condition. The resulting solution is mixed with a solution of ammonium thiocyanate in water and acetone, and the colour compared with that of a standard iron solution similarly treated. The ordinary ashing process is

thus eliminated, and the estimation requires only 0.040 c.c. of blood, and may be completed in ten to fifteen minutes.

H. W. B.

**Estimation of Chromium in the Presence of Iron.** K. SCHORLEMMER (*Collegium*, 1918, 145—149).—Iron salts must be removed previous to the estimation of chromium by means of thio sulphate. The solution is treated with hydrogen peroxide, heated, then cooled, and reoxidised by the addition of a further quantity of hydrogen peroxide; the ferric hydroxide is collected, dissolved in acid, twice oxidised with hydrogen peroxide, again collected, and the filtrate added to the first filtrate. The chromium is then estimated in the solution. A further treatment of the ferric hydroxide with hydrogen peroxide may be necessary if much iron is present.

W. P. S.

**Analysis of Molybdenum Ores containing Copper.** W. HOEFFNER and O. BINDER (*Chem. Zeit.*, 1918, 42, 315).—Small quantities of copper in an ammoniacal solution of molybdic acid cannot be precipitated by the addition of ammonium sulphide, since copper is soluble to the extent of 0.015 gram (or more) per 100 c.c. of the sulphide solution. To effect the separation of the copper, the ammoniacal solution should be acidified with sulphuric acid and the copper deposited electrolytically after the addition of nitric acid.

W. P. S.

**Isemannite.** H. F. TANCY (*Met. and Chem. Eng.*, 1918, (186)).—Isemannite is a blue compound of molybdenum soluble in water to which the formula  $\text{MoO}_2 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$  is usually given. The molybdenum, occurring as  $\text{MoO}_2$ , may be determined by extracting the ore with hot water, adding to the extract 25% by volume of hydrochloric acid and its own bulk of ether. The mixture is shaken and the layers separated, the aqueous layer being again treated with ether and the ethereal solutions combined. This ether extract is washed ten times with 10 c.c. of hydrochloric acid diluted with 25 c.c. of water to remove iron. The blue compound is titrated with  $N/100$ -permanganate in a sulphuric acid solution. The total molybdenum present is determined by fuming the solution with strong sulphuric acid, diluting it with water, and adding sodium hydroxide. A precipitate of the hydroxides of manganese and iron is filtered off, the filtrate acidified with 2.5% sulphuric acid, and passed while hot through a Jones reductor. F. C. TH.

**Estimation of Tungsten and Vanadium in the Presence of Titanium.** G. FENNER (*Chem. Zeit.*, 1918, 42, 403).—To separate tungsten from titanium in a mineral, the latter is fused with sodium peroxide, cooled, the fused mass boiled for a few minutes with water, and the solution then filtered; the titanium remains insoluble, whilst the tungsten passes completely into the filtrate. This method cannot be used for the separation of vanadium from titanium, since the greater part, if not all, of the vanadium remains insoluble. In this case, the mineral, after silica

has been removed by treatment with hydrofluoric acid and sulphuric acid, is fused with sodium pyrosulphate, the fused mass dissolved in dilute sulphuric acid, the solution filtered, and the filtrate treated with hydrogen peroxide until a distinct coloration has developed, an excess of the peroxide being avoided. Ammonium fluoride is then added; this destroys the yellow colour of the titanium compound, but does not affect the reddish-brown colour of the vanadium compound. After the yellow colour due to iron salts has been removed by the addition of phosphoric acid, the vanadium is estimated colorimetrically, using a standard prepared under the same conditions and as far as possible with the same quantities of reagents.

W. P. S.

**Quantitative Analysis of Vanadium Compounds with the Aid of Carbon Tetrachloride.**

PAUL JANNASCH and HENRY E. HARWOOD (*J. pr. Chem.*, 1918, [ii], 97, 93—137).—The application of carbon tetrachloride as a reagent for quantitative analysis (Jannasch and others, *A.*, 1913, ii, 876; 1910, ii, 1076; 1909, ii, 728, 767; 1908, ii, 685; 1907, ii, 864) is extended by its use for the estimation of vanadium in its compounds. The vanadium compound in a silica boat enclosed in a silica tube is heated in a current of carbon dioxide and carbon tetrachloride vapour, the resulting vanadium chlorides being collected by passage into dilute nitric acid and water successively. The vanadic acid solution thus obtained is reduced to vanadyl sulphate, the amount of which can then be estimated volumetrically with potassium permanganate. [See also *J. Soc. Chem. Ind.*, October.]

D. F. T.

**Application of Rapidly Rotating Metallic Reductors in the Estimation of Vanadic Acid.**

F. A. GOOCH and W. SCOTT (*Amer. J. Sci.*, 1918, [iv], 46, 427—436).—The reduction of vanadic acid in the presence of dilute sulphuric acid may be effected quickly by the aid of rapidly rotating anodes of silver or copper in an electrolytic cell or by a rapidly rotating cylinder of zinc, over-reduction being corrected by the addition of silver sulphate, which automatically forms vanadium tetroxide. The completion of the reduction is indicated by the appearance of precipitated silver in the solution. The reduced liquid is boiled to coagulate the silver, filtered, diluted, again heated to boiling, and titrated with potassium permanganate. The correction applied is variable when an electrode of commercial copper is used, but an electrode of silver plated with copper from a solution of copper sulphate, free from iron, is satisfactory. When zinc is the reducing agent, the results are comparable only if the volume and temperature of the solution, the relative size of the zinc cylinder, and its rate of rotation are kept constant.

A. B. S.

**Electroanalysis of Bismuth without Platinum Electrodes.**

PELAYO POCH (*Anal. Fis. Quim.*, 1918, 16, 520—533).—An account

of experiments on the estimation of bismuth in solution in nitric, tartaric, sulphuric, and acetic acids, and in ammoniacal solution. In each case, the estimation was carried out with platinum electrodes, with a platinum anode and a copper cathode, with a platinum cathode and an iron or graphite anode, and with a copper cathode and an iron or graphite anode.

A. J. W.

**The Copper Method for Estimating Glycerol.** F. L. WEISS (*Chem. Weekblad*, 1918, 15, 862—868).—There is no compound of copper and glycerol of constant composition, but the proportion of copper depends on four factors: (1) The proportion of glycerol in the solution, the amount of copper increasing with the glycerol. (2) Any rise of temperature, which lowers the proportion of copper, especially in very dilute solutions. (3) The degree of dilution of the liquid. (4) The concentration of the free alkali.

A. J. W.

**The Estimation of Phenol in "Cresylic Acid."** J. J. FOX and M. F. BARKER (*J. Soc. Chem. Ind.*, 1918, 37, 265—268r).—For the estimation of phenol in commercial 'cresylic acid' by the method previously described (A., 1917, ii, 513), a number of additional details are given. In place of ether, benzene may be used for getting rid of tar oils and bases, but since benzene is obstinately retained by the solution of the tar acids in sodium hydroxide solution, this solution must be heated sufficiently strongly before acidification to expel all the benzene. Benzene may also be used in place of ether to extract the tar acids after acidification, the washing and drying being carried out as described before. The neutral oils and bases may also be removed by dissolving the tar acids in sodium hydroxide solution and steam distilling, but care must be taken that the sodium hydroxide is in sufficient excess to prevent any tar acids, particularly *o*-cresol, being carried over with the steam.

A short method has been devised for determining whether a sample of 'cresylic acid' contains more than about 5% of phenol. The dried tar acids are fractionally distilled in the standard apparatus described, and the fraction distilling up to 210° is collected and redistilled. The portion boiling up to 202° is collected, and if this is less than 5% the sample is satisfactory. If it is more than 5% it is again distilled, and the fraction boiling up to 195° is collected and the phenol estimated by a specific gravity determination.

A bibliography of papers dealing with phenol and cresol estimations and separations is appended.

E. H. R.

**Chemical Diagnosis of Picric Jaundice. Possible Simulation of Bile Pigments in the Urine.** DOMENICO GANASSINI (*Boll. chim. farm.*, 1918, 57, 161—167).—The author describes methods of detecting the simulated catarrhal jaundice caused by the ingestion of picric acid by individuals (in Italy) wishing to

escape military service, these methods being modifications of Le Mithouard's reaction (*Presse médicale*, 1916, No. 27, 475), the triaminophenol reaction (compare Rodillon, A., 1915, ii, 805), and Derrien's diazo-reaction (*Presse médicale*, 1915, No. 35, 285) for the detection of picric acid derivatives in the urine. It is pointed out that Le Mithouard's reaction is given also by Martius-yellow and by naphthol-yellow S, the latter being a harmless colour allowable in food products; these colouring matters do not, however, respond to the other two reactions mentioned.

Only in exceptional cases of picric jaundice may the picramic acid in the urine be accompanied by bile pigments, this being so especially when large doses of picric acid have been ingested. It is found that the possibility exists of simulating the presence of bile pigments in a urine which does not contain them, for instance, by addition of either a pinch of antipyrine mixed with a trace of alkali nitrate or a very small quantity of Congo-red; a method is given for detecting this fraud, which may be practised to render the jaundice more certain.

T. H. P.

**Identification and Estimation of Potassium Guaiacolsulphonate.** SAMUEL PALKIN (*J. Ind. Eng. Chem.*, 1918, 10, 610-612).—Potassium guaiacolsulphonate as used in medicine is usually mixed with gums, resins, alkaloids, etc. To detect the presence of the sulphonate, the sample is treated with dilute hydrochloric acid, filtered, and a portion of the filtrate tested for sulphates before and after oxidation with sodium peroxide (in the acid solution); any increase in the quantity of sulphate after oxidation indicates the presence of a sulphonate. Another portion of the filtrate is rendered alkaline and treated with a drop of diazotised nitroaniline; a deep red coloration, changing to yellow when acidified, denotes the presence of guaiacolsulphonate. In the absence of much organic matter, a portion of the sample may be distilled with the addition of phosphoric acid and sodium chloride; the filtrate gives a green coloration with ferric chloride, and, when rendered ammoniacal, reduces silver nitrate. Potassium guaiacolsulphonate may be estimated from the amount of sulphuric acid formed when it is oxidised by repeated evaporation with bromine and nitric acid.

W. P. S.

**Estimation of Acetic Acid by Distillation with Phosphoric Acid.** W. FAITOUTE MUNN (*J. Ind. Eng. Chem.*, 1910, 10, 550-552).—For the estimation of acetic acid in calcium acetate residues, etc., the sample is distilled with the addition of dilute phosphoric acid, and the distillate is collected in a receiver containing an excess of standardised barium hydroxide solution. A current of air free from carbon dioxide is drawn through the apparatus during the distillation, and dilute phosphoric acid is admitted to the distillation flask at the same rate as that at which the liquid distils. When the distillation is completed (this requires

about ninety minutes), the contents of the receiver are titrated with  $N/10$ -hydrochloric acid, using phenolphthalein as indicator; this gives the excess of barium hydroxide. If any barium carbonate has formed, due to the presence of carbonates in the sample, the barium carbonate is dissolved by adding  $N/1$ -hydrochloric acid in slight excess and then titrating the excess with  $N/1$ -sodium hydroxide solution, using methyl-orange as an external indicator. Allowance is made for the quantity of carbonate thus found. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**The Detection of  $\delta$ -Glycuronic Acid and other Acids with similar Behaviour by the Naphtharesorcinol Reaction.**

A. W. VAN DER HAAR (*Biochem. Zeitsch.*, 1918, **88**, 205—212).—An application of Neuberg and Saneyoshi's modification of Tollens's reaction, as applied to plant products. The substance is first hydrolysed with 5% sulphuric acid, the mixture is then neutralised with barium hydroxide, and concentrated after filtration. Lead acetate is then added, and, after filtration, basic lead acetate; the glycuronate is contained in the precipitate thus produced, and this is then heated with 10 c.c. of 10% hydrochloric acid and 100 mg. of naphtharesorcinol for one minute. After cooling to  $50^{\circ}$ , benzene is added, and if glycuronic acid is present, this on shaking takes up a violet pigment, which gives a characteristic  $D$ -band of the spectrum. S. B. S.

**Estimation of Phthalic Anhydride in Crude Phthalic Acid.**

CHARLES R. DOWNS and CHARLES G. STUPP (*J. Ind. Eng. Chem.*, 1918, **10**, 596—598).—The sample is volatilised from a small glass capsule, and the volatilised phthalic anhydride collected in a tube containing cotton wool, the lower end of this tube being inserted in the neck of the capsule. The capsule is heated at  $220^{\circ}$ , and a current of air drawn through the apparatus during the operation. The cotton wool is then removed from the tube, boiled with an excess of standard sodium hydroxide solution for thirty minutes, the solution then treated with an excess of standard acid, again boiled, and titrated, using phenolphthalein as indicator. Each c.c. of  $N/10$ -sodium hydroxide solution is equivalent to 0.0074 gram of phthalic anhydride. The non-volatile residue remaining in the capsule may also be weighed. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

**Dropping-point Apparatus for the Examination of Fats, Waxes, and Bitumens.**

F. DUPRÉ (*Chem. Zeit.*, 1918, **42**, 398. Compare Ubbelohde, A., 1905, ii, 658).—The substance to be tested is placed in a small metal nipple which is attached to the bulb of a thermometer so that the lower part of the bulb is immediately above the surface of the substance. The thermometer is suspended in a test-tube, which is immersed in a heating-bath heated to about  $20^{\circ}$  below the probable dropping point of the

substance, and the temperature is raised at the rate of  $1^{\circ}$  per minute until a drop of the melted substance falls from the nipple.

W. P. S.

**Method for Estimating Citral. A Modification of the Hiltner Method.** C. E. PARKER and R. S. HILTNER (*J. Ind. Eng. Chem.*, 1918, 10, 608—610).—Some samples of lemon and orange oils and extracts yield a blue or green coloration when treated with *m*-phenylenediamine hydrochloride, thus limiting the applicability of Hiltner's method, which depends on the formation of a yellow coloration. The addition of oxalic acid, however, inhibits the production of the blue or green coloration, and it is recommended that the reagent be prepared as follows: One gram of *m*-phenylenediamine hydrochloride and 1 gram of crystallised oxalic acid are dissolved separately in 80% alcohol, the solutions are mixed, diluted to 100 c.c. with 80% alcohol, treated with Fuller's earth, and filtered.

W. P. S.

**Detection of Acetone.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, 55, 1021—1029).—Vanillin can replace salicylaldehyde in Frommer's test for acetone (*Berl. Klin. Wochenschr.*, 1902, 42, 1005) with similar results. The presence of acetaldehyde or formaldehyde is prejudicial.

A. J. W.

**Estimation of Acetone.** ALLAN J. FIELD (*J. Ind. Eng. Chem.*, 1918, 10, 552).—Messenger's volumetric method, depending on the formation of iodoform, was found to be untrustworthy; the use of arsenious acid in place of thiosulphate for the titration (compare Vaubel and Scheuer, A., 1905, ii, 291) yielded no advantage. Robineau and Rollin's method as modified by Kebler (*J. Amer. Chem. Soc.*, 1897, 19, 316) is the most trustworthy for the estimation of acetone; the results are not affected by the presence of alcohol or by differences in the time of shaking.

W. P. S.

**Method for the Separation and Quantitative Estimation of the Lower Alkylamines in the Presence of Ammonia.** F. C. WEBER and J. B. WILSON (*J. Biol. Chem.*, 1918, 35, 385—410).—The total volatile nitrogen is first estimated by distillation of the alkaline solution containing ammonia and the amines into 0.05*N*-acid, and titration of the excess of acid with 0.02*N*-alkali, using methyl-red as the indicator.

For the estimation of the total amines, a volume of the original solution containing an amount of total volatile nitrogen equivalent to from 40 c.c. to 60 c.c. of 0.05*N*-acid is placed in a 500 c.c. volumetric flask, diluted with water to within 20 c.c. of the mark, and treated with 10 c.c. of an alkaline mixture composed of equal parts of 20% sodium hydroxide and 30% sodium carbonate solutions. After making to the mark, 0.1 gram of yellow oxide of



mercury is added for each c.c. of 0.1*N*-acid equivalent to the total volatile nitrogen. The flask is covered with a black cloth and shaken for one hour. The solution is then filtered through a cotton filter under pressure, and two 200 c.c. portions of the filtrate are distilled into 25 c.c. of 0.05*N*-acid. The acid neutralised is equivalent to the amines present, from which the total amines may be calculated. The difference between the total volatile nitrogen and the total amines represents the *ammonia* nitrogen.

The distillate containing the total amines is acidified with 0.5 c.c. of concentrated sulphuric acid and evaporated to 35 c.c. It is transferred to a 50 c.c. flask and diluted with water to the mark. The *monoamines* are now estimated in 10 c.c. in the Van Slyke amino-nitrogen apparatus, using the mixing bulb of the large size apparatus and the measuring burette of the micro-apparatus. The remaining 40 c.c. are transferred to a 200 c.c. flask and treated with 20 c.c. of a saturated solution of sodium nitrite and 10 c.c. of glacial acetic acid. The liquid is shaken from time to time to remove as much gas as possible, and, after an hour, a drop of phenolphthalein indicator is added and 30 c.c. of a 20% sodium hydroxide solution. On mixing, the solution should remain acid; if it begins to turn red, a few drops of acetic acid are added. After a few hours, 15 c.c. to 20 c.c. more of the sodium hydroxide solution are added, and it is distilled into 25 c.c. of 0.05*N*-sulphuric acid. It is titrated back as before with 0.02*N*-alkali, using methyl-red as indicator. The acid used is equivalent to the *triamines*. The *diamines* may be estimated by difference, or by the following method. To the distillate containing the triamine (and also the diamine in the form of nitrosoamine) 10 c.c. of concentrated hydrochloric acid and a few grams of granulated zinc are added, and when hydrogen is being evolved freely it is placed over a small flame and heated to boiling. The solution is decanted from the remaining zinc, which is washed with three 10 c.c. portions of water. After addition of a drop of phenolphthalein and about 10 grams of sodium hydroxide, the product is distilled into 25 c.c. of 0.05*N*-acid, and titrated back as before. The acid used is equivalent to the sum of the diamines and triamines present.

The method appears to give accurate results, and may be employed in the analysis of fish products, putrid flesh, bad sausages, biological fluids, etc.

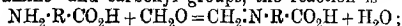
H. W. B.

**Evaluation of Hexamethylenetetramine Tablets.** W. O. EMERY and C. D. WRIGHT (*J. Ind. Eng. Chem.*, 1918, 10, 606-608).—A portion of the sample is boiled under a reflux apparatus with dilute hydrochloric acid, and the solution is then made up to a known volume. An aliquot portion of this solution is treated at 0° with alkaline potassium mercuric iodide solution (a modified Nessler reagent); the formaldehyde is oxidised to a formate, and an equivalent amount of metallic mercury is precipitated. The mixture is then acidified with acetic acid, and an excess of *N*/10-iodine solution added; the iodine combines with

the mercury, and the excess of iodine is titrated with thiosulphate solution. [See, further, *J. Soc. Chem. Ind.*, October.]

W. P. S.

**Abnormalities in the Formol Titration Method.** S. L. JONIDI (*J. Amer. Chem. Soc.*, 1918, **40**, 1031—1035).—An explanation is given of the abnormalities which sometimes render untrustworthy Sørensen's formaldehyde titration method of estimating amino-acids, polypeptides, etc. The function of the formaldehyde is to convert the basic nitrogen in the molecule into a neutral group, so that the carboxyl group can be accurately titrated; in the case of simple amino-acids,  $\text{NH}_2\cdot\text{R}\cdot\text{CO}_2\text{H}$ , containing only amino- and carboxyl groups, the reaction is



the group  $\text{CH}_2\cdot\text{N}\cdot$  is neutral, and the resulting monobasic acid contains no groups modifying its acidity. Proline, however, contains an imino-group, and reacts with formaldehyde to give methyleneproline containing the group  $\text{N}\cdot\text{CH}_2\cdot\text{N}\cdot$ , which is still somewhat basic, with the result that the formaldehyde method gives too low results. The same holds for hydroxyproline. The product from formaldehyde and histidine also contains the group  $\text{N}\cdot\text{CH}_2\cdot\text{N}\cdot$ , and the estimation is therefore low, but the result is better than in the case of proline, probably owing to the acidic nature of the azole nucleus. Tryptophan has not yet been estimated by Sørensen's method, but in view of the presence of an imino-group, it seems safe to predict that the result will be low. In the case of lysine, the method gives low results, although an accurate result would be expected, since the molecule contains, apart from the two amino-groups, no groups which could affect the carboxyl group; the discrepancy is attributed to the distance of the  $\omega$ -amino-group from the carboxyl group.

C. S.

**Analysis of Calcium Cyanamide containing much Dicyanodiamide and Urea.** E. HENE and A. VAN HAAREN (*Zeitsch. angew. Chem.*, 1918, **31**, 129—131).—A solution of the cyanamide, dicyanodiamide, and urea is prepared in the usual way, and an aliquot portion, containing about 0.2 gram of nitrogen, is diluted to 200 c.c. and treated with 20 c.c. of 10% silver nitrate solution and 30 c.c. of 10% potassium hydroxide solution; the precipitate, which contains all the cyanamide and dicyanodiamide and some of the urea, is washed, mixed with 150 c.c. of water, dissolved in the minimum quantity of nitric acid, diluted to 200 c.c., and 100 c.c. of this solution are treated with 2 c.c. of silver nitrate solution and 15 c.c. of potassium hydroxide solution. The precipitate, which now contains all the cyanamide and dicyanodiamide, is collected and the nitrogen in it determined by Kjeldahl's method. In another portion of the original solution, the cyanamide is precipitated by means of silver nitrate and ammonia, and the nitrogen determined in the precipitate; the difference between this and the first nitrogen determination gives the dicyanodiamide nitrogen.

The urea nitrogen is found from the difference between the sum of the cyanide and dicyanodiamide nitrogen and the total nitrogen in the sample. W. P. S.

[**Estimation of Creatinine in Blood.** I. CHERTKOV (*Rev. méd. suisse romande*, 1917, **37**, 748; from *Physiol. Abstr.*, 1918, **3**, 247).—Protein is precipitated by trichloroacetic acid; to the filtrate, sodium hydroxide and picric acid are added, and the creatinine is estimated colorimetrically. S. B. S.]

[**Estimation of Theobromine.** W. O. EMERY and G. C. SPENCER (*J. Ind. Eng. Chem.*, 1918, **10**, 605—606. Compare A., 1914, ii, 825).—A method for the estimation of theobromine, either alone or mixed with sodium acetate and sodium salicylate, depends on the formation of its periodide,  $C_7H_5O_2N_4, HI_4$ . A quantity of 0.1 gram of the sample (with an equivalent quantity of sodium acetate in the case of theobromine alone) is dissolved in 2 c.c. of glacial acetic acid, 5 c.c. of hot water are added, and the solution is transferred to a 100 c.c. flask containing 50 c.c. of  $N/10$ -iodine solution; 20 c.c. of saturated sodium chloride solution and 2 c.c. of concentrated hydrochloric acid are then added, and, after about eighteen hours, the mixture is diluted to 100 c.c., filtered, and the excess of iodine titrated in an aliquot portion of the filtrate. W. P. S.]

[**Method for making Electrometric Titrations of Solutions containing Protein.** JOHN C. BAKER and LUCIUS L. VAX SLYKE (*J. Biol. Chem.*, 1918, **35**, 137—145).—The apparatus consists of a wide-mouthed bottle, holding about 400 c.c., provided with a cork stopper containing perforations through which the several parts or connexions pass into the bottle. The hydrogen electrode, made of platinum foil, is suspended in a special manner inside the bell-shaped end of the tube carrying hydrogen, and is so arranged that it can be lowered into or drawn out of the solution titrated. Other parts are (a) a glass tube admitting the titration reagent from a burette into the solution titrated, (b) special stirring apparatus, (c) a tube for introducing additional reagents, (d) a tube containing potassium chloride, and, in addition, other pieces of apparatus required to measure the hydrogen-ion concentration.

In operating, the solution under examination is placed in the bottle, and hydrogen passed in, the electrode being above the solution. The stirrer being in motion, the electrode is lowered into the solution, electric connexions are made, equilibrium is established, and then the titration reagent run in. Readings of the *E.M.F.* are made once a minute until constant, and titration is then continued. The apparatus is designed to prevent local chemical action at the point where the reagent enters the solution under titration. H. W. B.]

LXXIV.—*The Relative Activity of certain Alkyl Iodides with Sodium  $\alpha$ -Naphthoxide in Methyl Alcohol.*

By HENRY EDWARD COX.

THE relative activities of methyl, ethyl, and *n*-propyl iodides with sodium naphthoxides in ethyl alcohol were discussed in a previous paper (this vol., p. 666), and attention was directed to the abnormal increase in activity of methyl iodide at high dilutions. The object of the present work was to examine similarly the reaction between methyl iodide and sodium  $\alpha$ -naphthoxide in methyl alcohol as solvent.

Menschutkin (*Zeitsch. physikal. Chem.*, 1890, **6**, 41) found that ethyl iodide and triethylamine react more rapidly in methyl alcohol than in ethyl alcohol, and ascribed this to the higher dielectric constant of the methyl alcohol. Hecht and Conrad (*ibid.*, 1889, **3**, 42) and Segaller (T., 1914, **105**, 112) have shown that sodium ethoxide and phenoxide react more rapidly in ethyl alcohol as solvent. This is surprising in view of the fact that Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474; T., 1914, **105**, 2582) have shown that in the case of the phenoxide, the activity due to ions is more than five times that due to the undissociated phenoxide. The activity would therefore be expected to be higher in the solvent of greater dissociating power, namely, methyl alcohol. Sodium  $\alpha$ -naphthoxide, like ethoxide and phenoxide, reacts about twice as fast with the alkyl iodides in ethyl alcohol as in methyl alcohol.

## EXPERIMENTAL.

The methyl alcohol was quite free from acetone, and was dehydrated over calcium oxide and calcium. The measurements were carried out at 40.0°, as described in the previous paper.

The following results were obtained with methyl iodide and sodium  $\alpha$ -naphthoxide in equivalent concentration. The third column gives the values of  $k_v$  calculated from the equation  $k_v = k_i + a \log v$ .

$$a = 0.00333.$$

$v$ .	$k_v$ (found).	$k_v$ (calc.).
1	0.01644	0.01644
2	0.01797	0.01744
4	0.01863	0.01844
8	0.01823	0.01845
16	0.02449	0.02045
32	0.03633	0.02145
64	0.04461	0.02245

These figures show that the above equation holds as far as  $v=8$ , and then  $k$ , increases abnormally rapidly, as was found to be the case in ethyl alcohol.

In order to determine whether the increase with dilution is mainly due to the change in concentration of the naphthoxide or of the methyl iodide, the following experiments were made with non-equivalent concentrations. The results are calculated from the usual formula,  $k = \frac{1}{(a-b)t} \log_e \frac{b(a-x)}{a(b-x)}$ , where  $a$  and  $b$  are the concentrations of iodide and naphthoxide respectively.

The results show that change in concentration of the alkyl iodide has comparatively little effect on the velocity constant, whereas the concentration of the naphthoxide has a very marked effect.

		$k$ .
N/16-Naphthoxide; N/4-Methyl iodide	N/8.	0.02243
	N/16. " "	0.02321
	N/16. " "	0.02449
N/8-Iodide	N/8-Naphthoxide	0.01923
	N/16. " "	0.02321
N/4-Iodide	N/4-Naphthoxide	0.01863
	N/16. " "	0.02449

On plotting values of  $k$  against  $\log v$ , there is a sharp curve upwards at the point corresponding with about  $v=8$ . It seemed possible that at higher dilutions the reaction might not be bimolecular, but of a higher order, due to the formation of additive compounds, such as  $C_{10}H_7ONa, nCH_3I$ , and in order to test this point, Ostwald's 'isolation' method was applied, as follows.

The reaction velocity may be represented by the equation  $-dc_1/dt = kc_1^m c_2^n$ , where  $c_1$  and  $c_2$  are concentrations of naphthoxide and iodide respectively. In the following experiments,  $c_2$  is large compared with  $c_1$ , and is taken as constant during that part of the reaction measured; the equation then takes the form  $-dc_1/dt = k_1 c_1^m$ , where  $k_1 = kc_2^n$ . The order of reaction is then equal to  $m$ .

Experiment I.			Experiment II.			Experiment III.		
N/16-Naphthoxide.			N/16-Naphthoxide.			N/16-Naphthoxide.		
N/1-Iodide.			N/4-Iodide.			N/8-Iodide.		
$t$ .	$c$ .	$1/t \log c_0/c$ .	$t$ .	$c$ .	$1/t \log c_0/c$ .	$t$ .	$c$ .	$1/t \log c_0/c$ .
0	6.45	—	0	7.30	—	0	7.60	—
30	3.70	0.00804	66	5.10	0.00236	77	6.10	0.00124
55	2.35	0.00797	83	4.75	0.00225	96	5.80	0.00122
65	2.00	0.00786	106	4.20	0.00226	130	5.35	0.00117
75	1.62	0.00800	143	3.50	0.00217	160	4.95	0.00116
Mean $k_1' = 0.00797$			Mean $k_1'' = 0.00224$			Mean $k_1''' = 0.00120$		

The values of  $k_1$  are sufficiently constant to show that the reaction is unimolecular with regard to the naphthoxide.

If  $k_1'$  and  $k_1''$  are values of  $k_1$  from two experiments in which the concentration of naphthoxide is initially the same, whilst that of the methyl iodide is varied and equal to  $c_2'$  and  $c_2''$ , then  $k_1' = k c_2'^n$  and  $k_1'' = k c_2''^n$ , hence  $n = \log \frac{k_1'}{k_1''} \bigg/ \log \frac{c_2'}{c_2''}$ . Substituting the values obtained in experiments I, II, and III,  $n = 0.92, 0.91, 0.90$ , which indicates that  $n$  approaches the value unity. The reaction is therefore unimolecular with respect to methyl iodide, and the whole reaction is bimolecular at all dilutions from  $N/1$  to  $N/64$ .

*Effect of the Products of Reaction on the Velocity Coefficient.*

Arrhenius, and more recently Senter, have pointed out that velocity coefficients often exhibit a tendency to fall off as the experiment proceeds, owing to the action of the salts formed during the reaction. As the constants in the reactions here considered show this tendency to diminish, the following experiments were made with an addition of anhydrous sodium iodide and  $\alpha$ -naphthyl methyl ether respectively.

<i>N/8</i> -Sodium $\alpha$ -naphthoxide and <i>N/8</i> -methyl iodide.	<i>k</i> .
No sodium iodide .....	0.01923
<i>N/4</i> " " .....	0.01929
<i>N/8</i> " " .....	0.01907
<i>N/8</i> $\alpha$ -Naphthyl methyl ether .....	0.01690
<i>N/4</i> -Naphthoxide and <i>N/4</i> -methyl iodide.	
No $\alpha$ -Naphthyl methyl ether .....	0.01863
<i>N/4</i> - " " " " .....	0.01535

These results show that whilst sodium iodide has no appreciable influence on the velocity coefficient, the formation of the ether greatly retards the velocity, and this probably accounts for the observed falling off of the velocity constant.

It is still unexplained why the velocity is practically constant throughout any one experiment, although the concentration falls to less than one-half of its initial value, whereas if an experiment is commenced at a lower concentration, the velocity coefficient is considerably increased in accordance with the equation  $k_v = k_1 + a \log v$ .

*Ethyl and n-Propyl Iodides.*

These iodides react more slowly than methyl iodide, and the equation  $k_v = k_1 + a \log v$  is found to hold to as high a dilution as it was practicable to measure.

The results of three experiments are as follows:

	Ethyl iodide.		n-Propyl iodide.	
v.	$k_2$ (found).	$k_2$ (calc.).	$k_2$ (found).	$k_2$ (calc.).
1	0.006350	0.006350	0.002355	0.002355
8	0.006026	0.005982	0.003071	0.003077
32	0.006280	0.006403	0.003801	0.003559
	$a = 0.00070$		$a = 0.00080$	

The relative activities of the three iodides at concentration  $N/1$  are:

Solvent :—	Methyl alcohol.	Ethyl alcohol.
Methyl iodide .....	6.98	9.55
Ethyl iodide .....	2.27	2.14
n-Propyl iodide .....	1.00	1.00

and the ratio of the velocity coefficients in these two solvents is:

	Methyl iodide.	Ethyl iodide.	n-Propyl iodide.
Methyl alcohol ...	1.00	1.00	1.00
Ethyl alcohol.....	2.50	1.71	1.83

These figures agree very closely with the results of Hecht and Conrad and of Segaller for sodium ethoxide and phenoxide.

### Summary and Conclusions.

(1) The reaction between methyl iodide and sodium  $\alpha$ -naphthoxide is bimolecular at all dilutions from  $N/1$  to  $N/64$ . The velocity coefficient increases with dilution in accordance with the equation  $k_v = k_1 + a \log v$  as far as  $v=8$ , and thereafter it increases more rapidly.

(2) The effect of varying the concentration of the alkyl iodide is comparatively small, but the initial concentration of the naphthoxide has a very marked effect on the velocity coefficient.

(3) Sodium iodide has no effect on the velocity coefficient.

(4)  $\alpha$ -Naphthyl methyl ether greatly retards the reaction.

(5) The velocity of reaction of the alkyl iodides is approximately twice as great in ethyl alcohol as in methyl alcohol.

(6) The relative activity of the first three members of the series is in the order methyl, ethyl, *n*-propyl iodide, and methyl iodide is much more active than the others.

I wish to express my thanks to Mr. G. R. Thompson for providing every facility for this work, and to Dr. J. C. Crocker for his interest and advice.

DOCK STREET,  
NEWPORT, MON.

[Received, August 29th, 1918.]

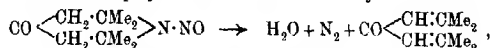
LXXV.—*The Hydrolysis of Soap Solutions, Measured by the Rate of Catalysis of Nitrosotriacetoneamine.*

By JAMES WILLIAM MCBAIN and THOMAS ROBERT BOLAM.

THE concentration of hydroxyl ion in soap solutions was measured by McBain and Martin (T., 1914, 105, 957) by the electromotive force method, and the measurements recorded in the present paper agree with those results in showing that the concentration of hydroxyl ion is only of the order of magnitude of  $N/1000$ . It is therefore impossible to attribute the conductivity of soap solutions to free hydroxyl ions. For the evidence with regard to the existence and nature of the ionic micelle and their bearing on the conductivity, reference should be made to other communications from this laboratory.\*

*Method of Measurement.*

The method employed was the rate of catalysis of the reaction



as shown by Francis and his collaborators (T., 1912, 101, 2358; 1913, 103, 1722; 1915, 107, 1651). The reaction is unimolecular and the velocity is proportional to the concentration of hydroxyl ion. The volume method had been found to be accurate to within about 2 or 3 per cent. at the ordinary temperature.

The results are calculated according to the system proposed by McBain (*Trans. Faraday Soc.*, 1917, 13, 1), which consists in always setting the rate constant equal to unity and in choosing the unit of time accordingly.

The formula used here is consequently

$$T = 2.303 \log \frac{A}{A-x},$$

instead of the hitherto customary

$$k = \frac{2.303}{t} \log \frac{A}{A-x}$$

where  $k$  is the rate constant. The disadvantages of the system hitherto employed, as compared with that proposed, are illustrated

\* McBain and Taylor, *Ber.*, 1910, 43, 321; *Zeitsch. physikal. Chem.* 1911, 76, 179; Bowden, T., 1911, 99, 191; McBain, Cornish, and Bowden, T., 1912, 101, 2042; Bunbury and Martin, T., 1914, 105, 417; McBain and Martin, T., 1914, 105, 957; Laing, T., 1918, 113, 435; McBain and Salmon, *J. Amer. Chem. Soc.*, 1918; McBain, *J. Soc. Chem. Ind.*, 1918, 37, 249 (a brief summary).



by the rate of reaction in the presence of  $0.0138N\text{-OH'}$  at  $40.0^\circ$ . The rate constant is  $0.0708$ . This statement is meaningless until the further information is given that "time has been measured in minutes." Under the new system, this becomes—"the time unit is  $14.1$  minutes"—a statement which is much more readily visualised, is self-contained, and does away with small decimals. It further means, in the case of unimolecular reactions such as the present, that the reaction requires  $14.1$  minutes to proceed to the extent of  $63.2$  per cent.

Determinations were made at  $30^\circ$ ,  $40^\circ$ ,  $70^\circ$ , and  $90^\circ$ . The values of the time units for definite concentrations of hydroxyl ion at each temperature were measured by observing the rate in solutions of sodium hydroxide. These solutions were made up from sodium and boiled-out conductivity water, and all vessels were carefully flushed out with air freed from carbon dioxide. Soap solutions were made up in silver vessels as described in previous communications. The reaction was carried out in a Jena-glass flask containing a small glass tube, which could be dropped into the solution in the flask when it was desired that the reaction should commence. In some cases this tube contained the soap solution, in others the solution of nitrosotriacetoneamine.  $0.1300$  Gram of that substance was employed in each case. The amount of gas which should have been evolved, saturated with water vapour at about  $18^\circ$ , is  $17.18$  c.c.; as a matter of fact, on the average about  $8$  per cent. more than this was evolved. Francis and Clibbens state that they obtained values within  $2.5$  per cent. of the theoretical volume. Hence the "infinity reading" was taken after a period five times as long as that required for the production of  $9.3$  c.c. of nitrogen.

The results for sodium hydroxide are given in table I, in the final column of which the product of "time unit" and concentration is recorded. This should be a constant for each temperature, and is also equal to the reciprocal of the older expression  $k/\text{OH'}$ . The final products for  $40^\circ$ ,  $70^\circ$ , and  $90^\circ$  are  $0.196$ ,  $0.0236$ , and  $0.00545$ , respectively. The degree of accuracy is much less at the higher temperatures, owing to the great speed of the reaction and the very low concentrations of hydroxyl ion, which alone are measurable. Further, the solubility of the glass and difficulties due to vaporisation and fluctuations of temperature play an increasing rôle. However, none of these influences vitally affects the value of the results, on account of the fact that the hydrolysis of the soaps is itself so small.

TABLE I.

*Rate of Catalysis in Solution of Sodium Hydroxide.*

Temperature.	Concentrations.		Number of experiments.	Time units <i>T</i> minutes.			C.T.
	NaOH <sub>18</sub>	OH <sup>-</sup> =C.		Max.	Min.	Mean.	
40°	0.0146	0.0139	4	14.4	13.5	14.1	0.196
70	0.00314	0.00302	4	8.32	8.80	7.67	0.0232
"	0.00392	0.00396	2	6.52	6.45	6.49	0.0244
90	0.000654	0.000626	2	9.43	9.01	9.22	0.00579
"	0.000785	0.000757	2	7.69	7.46	7.57	0.00569
"	0.000796	0.000766	2	6.41	6.33	6.37	0.00488

The temperature coefficient of the reaction above 40° is 2.02 and 2.04, depending on whether the time unit at 70° or 90° is taken for the calculation. This is in general agreement with the results previously and subsequently obtained (T., 1915, 107, 1657), showing that the temperature coefficient diminishes with rise of temperature.

*Applicability of the Method.*

In view of the low values of hydroxyl ion obtained for soap solutions, it was considered advisable to carry out a few experiments in order to determine the neutral salt action, if any, of the sodium salt by the lowest fatty acid of this series, namely, sodium acetate.

The results of two series of experiments are given in table II, where concentrations are expressed in volume normality at 90°. The first column gives the preparation used (*A* being sodium acetate made anhydrous by heating in an air-bath at 125°, *C* and *D* being ordinary crystals weighed either dry or moist after re-crystallisation and subsequently analysed, thus avoiding any slight loss of acetic acid through heating), the last column being the apparent hydroxyl-ion concentrations as deduced from the factors obtained from table I.

TABLE II.

*Sodium Acetate at 90° with and without Sodium Hydroxide.*

NaAc.	Concentrations.		Number of experiments.	Time units minutes.			(OH) <sub>9</sub> .
	NaAc.	NaOH.		Max.	Min.	Mean.	
<i>D</i> ) <i>C</i> )	0.923	—	2	28.1	25.5	26.8	0.000203
<i>A</i> ) <i>C</i> )	0.967	—	2	25.0	24.4	24.7	0.000221
<i>D</i> ) <i>A</i> )	0.923	0.000759	3	10.4	9.0	9.81	0.000556
	0.967	0.000759	2	9.7	8.9	9.32	0.000585

These results require elucidation, for there are two factors involved, namely, neutral salt action and hydrolytic equilibrium. Taking first hydrolysis, calculation shows that the observed rate of catalysis would indicate a rather high value,  $60-70 \times 10^{-14}$ , for  $K_w$ , the dissociation constant of water at  $90^\circ$ . The latter is still uncertain as between the limits  $33-70 \times 10^{-14}$ . With the present method, dilute solutions would have to be employed to minimise neutral salt action.

The nature of the neutral salt action follows from the experiments in table II, employing added sodium hydroxide. The sodium hydroxide added will, of course, be only moderately dissociated in accordance with the principle of isohydrism. The total rate predicted will consequently be less than that of the hydroxide when taken alone, in spite of the influence of hydrolysis. Taking one set of assumptions in the preceding paragraph, the hydroxyl ion predicted is about 0.000614 for both the 0.923 and 0.967*N*. solutions containing sodium hydroxide. Taking another set, using osmotic data, this number becomes about 0.000571, which is identical with the mean of the observed value in table II.

This suffices to show that sodium acetate in normal solution does not exhibit any accelerating neutral salt effect. If it has any effect, it retards the reaction by anything up to 6 per cent., which is within the experimental error for the calculation above.

A much more vital effect would be if the soap in concentrated solutions sorbs nitrosotriacetoneamine, thus cutting down the effective concentration at any time, and therefore the rate. The reaction would proceed to completion, for the whole of the amine would be liberated progressively, but the apparent rate would be proportionately less than that corresponding with the real concentration of hydroxyl ion. The whole of the nitrogen is actually evolved.

If this phenomenon occurs, it would be of importance only in concentrated solutions, where the soaps exist as colloidal electrolytes. There the apparent concentration of hydroxyl ion would be too small, whereas in dilute solutions, in which the soaps exist essentially as simple electrolytes, normal values would be observed.

This is just what is found when the results from the present method are compared with those from the determination of electromotive force (*loc. cit.*). The values are nearly identical up to *N*/20-solution, but at *N*/10-solution they begin gradually to diverge until at 0.8*N*-solution the alkalinity measured by catalysis is only a fraction of that found by the method of electromotive force.

The only uncertainty in the measurements from electromotive

force is in calculating the diffusion potential. If the difference between the methods is to be ascribed to this source, it would make the hydrolysis much smaller even than that deduced, which was one or two tenths of a per cent. This establishes even more conclusively the main result of the previous paper. This assumption, however, predicates that the palmitate micelle possesses only low equivalent mobility, whereas the high observed conductivity necessitates the opposition conclusion. If sorption is taken into account, the results obtained by the catalytic method confirm those derived from electromotive force.

Direct proof of the occurrence of sorption in concentrated solution is obtained by adding a known amount of sodium hydroxide to the soap and observing that the effect on the rate is abnormally low. This is not due to sorption of the hydroxyl ion by the soap, as both electromotive force data (*loc. cit.*) and other evidence show that basic soaps are not formed. Experiments of this kind are set forth in table III. The concentrations of sodium palmitate are given in weight normality, the sodium hydroxide in volume normality at 90°. Two experiments from table I are added for comparison. The results show strikingly that the apparent rate is much lower than that corresponding with the alkali present and added, which points to sorption of amine by soap in concentrated solution as the explanation of the low rate. It should be remembered, of course, that in these soap solutions the concentration of sodium ions is about 0.30 weight normal, or about 0.25 volume normal at 90°, so that the sodium hydroxide is not fully dissociated and the hydrolysis of the soap has been partly repressed. Even so, the observed rate is but a fraction of that expected.

The last three lines of table III present experiments carried out by J. C. Pope in June, 1918, using a special preparation of sodium palmitate, which, although discoloured, was found to be very slightly alkaline in 90 per cent. alcoholic solution. The rate in mixtures containing considerable excess of alkali is about six times less than if the soap had been absent. This confirms the conclusions already drawn and reconciles the results of the catalytic and electromotive force methods set forth in table IV.

TABLE III.

0.8 Sodium Palmitate at 90° with and without Sodium Hydroxide.

Concentration.		Number of experi- ments.	Time units minutes.			(OH').
NaP.	NaOH.		Max.	Min.	Mean.	
0.8	—	3	25.0	19.9	21.6	0.000252
"	0.000774	3	20.7	18.9	19.8	0.000275
"	0.000785	2	7.69	7.46	7.57	0.000784
1.0	—	2	15.0	14.8	14.9	0.000266
"	0.00374	1	—	—	8.09	0.000614
"	0.0187	1	—	—	1.75	0.00312

*Results with Soap Solutions.*

Measurements on solutions of pure palmitate have been carried out at 30°, 40°, 70°, and 90°. The results for sodium palmitate are given in table IV, and those for potassium palmitate in table V.

TABLE IV.

*Alkalinity of Solutions of Sodium Palmitate.*

Tem- pera- ture.	Con- centra- tion : weight nor- mality.	Number of experi- ments.	Time units minutes.			(OH').	Hydro- lysis, per cent.	By E.M.F., per cent.
			Max.	Min.	Mean.			
70°	0.046	4	43.7	42.0	42.8	0.000438	0.99	—
"	0.101	2	43.5	42.6	42.0	0.000561	0.59	—
90	0.042	2	6.02	5.98	6.0	0.000908	2.24	2.3
"	0.50	2	27.0	27.0	27.0	0.000202	0.05	0.37
"	0.8	3	25.0	19.9	21.6	0.000252	0.04	0.28

TABLE V.

*Alkalinity of Solutions of Potassium Palmitate.*

Tem- pera- ture.	Con- centra- tion : weight nor- mality.	Number of experi- ments.	Time units minutes.			(OH').	Hydro- lysis, per cent.	by E.M.F., per cent.
			Max.	Min.	Mean.			
30°	0.050	2	561.6	520.6	541.1	0.00097*	2.04	—
40	0.051	2	598.8	431.0	514.9	0.000391	0.82	—
70	0.050	3	43.7	42.6	43.1	0.000545	1.14	—
"	0.100	2	38.8	38.3	38.5	0.000612	0.65	—
"	0.85	4	409.9	380.2	395.1	0.0000594	0.009	—
90	0.019	3	7.4	7.0	7.2	0.000757	4.1	5.7
"	0.042	2	6.06	5.7	5.9	0.000928	2.3	2.2
"	0.1	4	8.1	5.7	5.9	0.000927	0.99	1.25
"	0.302	5	12.7	6.1	9.4	0.000580	0.22	0.64
"	0.85	1	—	—	49.5	0.000110	0.017	0.27

\* These experiments were carried out by F. H. Geake by the pressure method. As the solutions have begun to be heterogeneous the alkalinity is, as expected, greater than at the higher temperatures where it is liquid. Compare McBain and Martin, *loc. cit.*, p. 975.

The seventh column gives the concentration of hydroxyl ion deduced, neglecting the effect of sorption of amine, and in the eighth the percentage hydrolysis found by electromotive force measurements (*loc. cit.*) is added for comparison.

Comparison of the last two columns in tables IV and V brings out the agreement of the two methods for dilute solutions, whilst the divergence in the concentrated solution is due to sorption of amine by the colloidal soap, as already explained.

The tables show at once that the alkalinity of all soap solutions is low and cannot account for more than a few per cent. of the conductivity of soaps except in very dilute solutions. However, it is quite sufficient to exclude the existence of free palmitic acid in soap solutions except in very minute amount (see McBain and Martin, *loc. cit.*, p. 973). Since the concentration of the hydroxyl ion exceeds 0.00002*N* in the case of every soap solution, even when containing excess of fatty acid, all higher fatty acids which are formed or added must exist in the form of acid soap, that is, in solid solution, adsorbed or chemically combined, but not in the free condition, except to an immeasurably small extent. This combats a very prevalent error (see, for instance, Washburn, "Principles of Physical Chemistry," 1915, p. 379).

Potassium palmitate when studied by the method of electromotive force exhibits a maximum alkalinity equal to 0.000316*N* in 0.5*N*-solution, diminishing to a quarter of this value in 1.00*N*-solution, which corresponds with only 0.08 per cent. hydrolysis. The data for sodium palmitate were less definite, but it was shown (*loc. cit.*, p. 973) that the values in concentrated solution tend to be too high. This effect also helps to explain the divergence between the two methods in concentrated solutions. The falling off in absolute alkalinity is quite simply explained on the basis of McBain and Salmon's theory of colloidal electrolytes (*J. Amer. Chem. Soc.*, 1918), for in concentrated solutions the palmitate ions largely disappear, being displaced by the ionic micelle.

A word is necessary with regard to what we have called "hydrolysis, per cent.," in the last two columns of tables IV and V, for which we have been criticised by Bancroft (*Trans. Amer. Electrochem. Soc.*, 1915, 27, 184). Bancroft's criticism arises from our having regarded alkalinity (concentration of hydroxyl ion) as hydrolysis. The difference is largely a matter of words and of point of view. His contention is that the hydrolysis may have been anything up to 100 per cent., but that the hydroxyl ion has been immediately and almost quantitatively sorbed by the resulting acid palmitate (it cannot be palmitic acid, and the colloidal sodium palmitate must contain all the excess of palmitic acid liberated).

McBain and Martin's paper contains direct measurements of the alkalinity of sodium hydroxide in the presence of soap; the hydroxide shows no appreciable sorption by soap; this is direct experimental evidence which has apparently not been considered by Bancroft, and would appear to be conclusive.

*Summary.*

Rate of catalysis, like electromotive force, shows that soap solutions are definitely, although very slightly, alkaline.

This alkalinity decreases with falling temperature, but is increased again when the solution solidifies or becomes heterogeneous.

The concentration of hydroxyl ion observed in all cases is sufficient to exclude the widely held view of the possibility of the existence of appreciable amounts of free fatty acid in any soap solution. Instead, acid soap must be formed in which practically all the excess of fatty acid is sorbed or combined.

The experiments here communicated are taken from a series that had to be discontinued in July, 1914. Our thanks are due to the Colston Society of the University of Bristol for a grant which has defrayed the expenses of this investigation.

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LXXVI.—*Studies in the Phenylsuccinic Acid Series.*

*Part VII. The Action of Alcohols and Amines  
on *r*-Diphenylsuccinic Anhydride.*

By HENRY WREN and HOWELL WILLIAMS.

THE present investigation was undertaken with the primary object of ascertaining whether derivatives of *mesodiphenylsuccinic acid* are produced during the reaction of alcohols and amines with *r*-diphenylsuccinic anhydride. It has been pointed out previously by Anschütz and Bendix (*Annalen*, 1890, **259**, 73) that the *r*-anhydride is converted by hot water into a mixture of the *r*-acid (about 96 per cent.) and *meso*-acid (about 4 per cent.), and this result is corroborated by the observation of Wren and Still (T., 1915, **107**, 1451) that the optically active anhydrides, when treated

with hot water, pass into diphenylsuccinic acids of the same sign containing about 8 per cent. of optically inactive material, from which *mesodiphenylsuccinic acid* can be isolated in very small quantity. The action of cold ethyl alcohol on the *L*-anhydride gave a rather more complex result. About 20 per cent. of inactive material appeared to be present in the crude product, from which however, a homogeneous substance could not be isolated; after crystallisation from light petroleum, a small quantity of substance was obtained which was not completely molten below 146°. Since ethyl hydrogen *L*-diphenylsuccinate melts at 113.5–114.5°, whilst Franchimont (*Ber.*, 1872, 5, 1050) gave 140° as the melting point of the corresponding *r*-ester, it seemed valid to conclude that ethyl hydrogen *mesodiphenylsuccinate* was also present. A not dissimilar result is recorded by Anschütz and Bendix (*loc. cit.*), who, by shaking *r*-diphenylsuccinic anhydride with chloroform containing ethyl alcohol, obtained a product analyses of which gave results in agreement with those required for the ethyl hydrogen ester, but the physical constants (melting point of crop, 164–168°; melting point of substance from mother liquor, 156–174°) appeared to show that the material was not uniform.

The experiments just quoted pointed thus to a very profound influence of the reagent on the mode of opening of the anhydride ring, but their significance was greatly discounted by the incidental observation that ethyl hydrogen *r*-diphenylsuccinate melts at 170–171° instead of at 140°, as recorded by Franchimont. The action of *r*-diphenylsuccinic anhydride on methyl and ethyl alcohols, on aniline, and on *p*-toluidine has therefore been studied, with the result that in the case of ethyl alcohol only has any definite evidence of the formation of *meso*-derivatives been obtained, and even in this instance the amount is very small.

The interaction of *r*-diphenylsuccinic anhydride and aniline has been studied by Anschütz and Bendix (*Annalen*, 1890, 259, 92), who prepared diphenylsuccinanil by heating the anhydride with half its weight of aniline at 170–175°; on treatment with a boiling aqueous solution of barium hydroxide, the anil was converted into a diphenylsuccinanilic acid which melted at 220°. By the action of the anhydride on aniline dissolved in benzene, they isolated a substance which melted at 65–68°, resolidified at 105–108°, and again melted at 220°. A repetition of the latter experiment has led to a somewhat different result, since we find the crude product to melt at 173–176°, to resolidify at about 187°, and to melt again at 226°, the initial melting point, however, being somewhat dependent on the conditions of the determination; after purification, it yields a diphenylsuccinanilic acid



which melts at 173—175° with the evolution of gas, then re-solidifies, and again melts at 227°. This appears to be practically the sole product of the change. It is readily transformed into diphenylsuccinyl either by the action of heat or by ethyl-alcoholic hydrogen chloride. Considering the conditions of their formation, it appears not unreasonable to regard the product melting at 173—175° as derived from the *r*-acid and that melting at 220° as belonging to the *meso*-series.

*r*-Diphenylsuccinic anhydride reacts very readily with a solution of *p*-toluidine in benzene, giving an almost quantitative precipitate of an acid melting at 195—196°, which appears to be the sole product of the action. This acid yields a barium salt which is sparingly soluble in water; it is readily transformed by the action of heat or of alcoholic hydrogen chloride into diphenylsuccino-*p*-tolil. The latter substance is converted by alkali into a mixture of acids which can be separated by taking advantage of the widely differing solubilities of their barium salts in water; from the less readily soluble portion, the acid melting at 195—196° can easily be isolated, whilst the more readily soluble portion yields an isomeric acid melting and decomposing at 206°, which is easily converted into diphenylsuccino-*p*-tolil. From the mode of formation, the relatively lower melting point and sparing solubility of the barium salt, it appears reasonable to conclude that the former acid belongs to the racemic series, the latter being therefore a derivative of the *meso*-type.

#### EXPERIMENTAL.

##### *Partial Esterification of r- and meso-Diphenylsuccinic Acids.*

Ethyl hydrogen *mesodiphenylsuccinate* was obtained from the products of the incomplete esterification of the *meso*-acid by ethyl alcohol and sulphuric acid according to the Fischer-Speier method. Isolation was readily effected by shaking the crude product, obtained after removal of excess of alcohol, with water and chloroform, whereby unchanged *meso*-acid remained undissolved. The chloroform solution was agitated with concentrated sodium carbonate solution; the latter, when acidified, yielded an immediate precipitate of ethyl hydrogen *mesodiphenylsuccinate*, which was purified by crystallisation from slightly aqueous alcohol and subsequently from benzene.

*Ethyl hydrogen mesodiphenylsuccinate* separates from benzene in minute, colourless needles. It is readily soluble in cold chloroform or ether or in hot ethyl alcohol, and moderately so in cold ethyl alcohol. When heated, it shrinks to a thin core and melts

sharply at 174.5–175°. After being dried in a vacuum over calcium chloride, the ester retains half a molecule of water:

0.1461 gave 0.3765  $\text{CO}_2$  and 0.0816  $\text{H}_2\text{O}$ .  $\text{C}=70.3$ ;  $\text{H}=6.3$ .

0.5431 lost 0.0149 at 100–105°.  $\text{H}_2\text{O}=2.74$ .

0.1393 \* gave 0.3700  $\text{CO}_2$  and 0.0756  $\text{H}_2\text{O}$ .  $\text{C}=72.4$ ;  $\text{H}=6.1$ .

0.3885 neutralised 12.9 c.c. of 0.1033 *N*-sodium hydroxide.

Calc.: 12.64 c.c.

$\text{C}_{18}\text{H}_{18}\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{C}=70.3$ ;  $\text{H}=6.3$ ;  $\text{H}_2\text{O}=2.93$  per cent.

$\text{C}_{18}\text{H}_{18}\text{O}_4$  requires  $\text{C}=72.5$ ;  $\text{H}=6.1$  per cent.

Ethyl hydrogen *r*-diphenylsuccinate was similarly obtained by the incomplete esterification of *r*-diphenylsuccinic acid, and was purified through the sparingly soluble sodium salt, and finally by cautious crystallisation of the acid ester from a small quantity of ethyl alcohol. It may be more readily crystallised from aqueous alcohol or from a mixture of benzene and light petroleum (b. p. 80–100°), but the removal of small quantities of admixed *r*-acid is not easily accomplished in this manner.

Ethyl hydrogen *r*-diphenylsuccinate separates from alcohol in aggregates of ill-defined needles; it is readily soluble in the boiling, fairly readily so in the cold solvent. It dissolves readily in cold ether, fairly readily in cold benzene, sparingly in light petroleum. It melts at 170–171°:

0.4137 neutralised 13.9 c.c. of *N*/10-potassium hydroxide.

Calc.: 13.88 c.c.

0.1725 gave 0.4575  $\text{CO}_2$  and 0.0944  $\text{H}_2\text{O}$ .  $\text{C}=72.3$ ;  $\text{H}=6.1$ .

$\text{C}_{18}\text{H}_{18}\text{O}_4$  requires  $\text{C}=72.5$ ;  $\text{H}=6.1$  per cent.

On complete esterification with ethyl alcohol and sulphuric acid, the acid ester was converted into ethyl *r*-diphenylsuccinate melting at 84.5–85.5°, thus confirming the position of the ester in the racemic series.

Sodium ethyl *r*-diphenylsuccinate separates from water, in which it is sparingly soluble at the ordinary temperature, in aggregates of fine needles:

0.2188 † lost 0.0395 at 100–110°.  $\text{H}_2\text{O}=18.65$ .

$\text{C}_{18}\text{H}_{17}\text{O}_4\text{Na} \cdot 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=18.37$  per cent.

0.1788 ‡ gave 0.0386  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=6.89$ .

$\text{C}_{18}\text{H}_{17}\text{O}_4\text{Na}$  requires  $\text{Na}=7.20$  per cent.

The salt evolved acid fumes and became discoloured at 180°.

Barium ethyl *r*-diphenylsuccinate was prepared by neutralising a suspension of the ethyl hydrogen ester in water with barium hydroxide solution; it is moderately soluble in cold water:

\* Dried at 100–105° until constant in weight.

† Air-dried.

‡ Dried at 100–110°.

0.3754 \* lost 0.0177 at 100—110°.  $H_2O = 4.72$ .

$C_{36}H_{34}O_8Ba \cdot 2H_2O$  requires  $H_2O = 4.70$  per cent.

0.2034 † gave 0.0662  $BaSO_4$ .  $Ba = 19.12$ .

$C_{36}H_{34}O_8Ba$  requires  $Ba = 18.78$  per cent.

*Action of Ethyl Alcohol on r-Diphenylsuccinic Anhydride.*

r-Diphenylsuccinic anhydride (8.1 grams) was allowed to remain in a stoppered flask, with occasional shaking, with ethyl alcohol (100 c.c.) until solution was complete, for which about three days were required. (A small portion of the solution was evaporated to dryness, and the residue was titrated with standard sodium hydroxide solution; the results indicated that the ethyl hydrogen ester contained a very small proportion of the free acid. This experience was confirmed in a number of other instances, and it therefore appears to be a matter of very considerable difficulty to prepare the alcohol absolutely free from moisture and to maintain it in this condition during the experiment.) The alcoholic solution was concentrated and exactly neutralised with aqueous-alcoholic sodium hydroxide solution. After complete removal of the alcohol, the aqueous solution was cooled, when sodium ethyl r-diphenylsuccinate was readily deposited (crop A). The precipitate was removed, and a second small crop of crystals was obtained by concentrating the filtrate. The mother liquor from the latter crop was acidified with hydrochloric acid and extracted with ether. The ethereal extract, after evaporation, left a small residue which melted indefinitely at 148—200°. It was completely esterified with ethyl alcohol and sulphuric acid; the mixture of normal esters was crystallised from ethyl alcohol, when ethyl mesodiphenylsuccinate (about 0.4 gram) was obtained in well-defined needles which melted at 140—141°.

The crop A (see above) was decomposed with dilute hydrochloric acid; the precipitated acid ester (6.8 grams) melted sharply at 170—171°, and was in all respects identical with ethyl hydrogen r-diphenylsuccinate obtained by partial esterification of the r-acid.

*Action of Methyl Alcohol on r-Diphenylsuccinic Anhydride.*

r-Diphenylsuccinic anhydride (5 grams) was warmed with absolute methyl alcohol (40 c.c.) at 40° during six hours. The mixture was cooled and the precipitated acid ester removed; it melted at 196—198°, and proved to be pure methyl hydrogen r-diphenylsuccinate. The material obtained by evaporation of the filtrate melted at 194—198°; the esterification of the latter was completed

\* Air-dried.

† Dried at 100—110°.

as usual, but the only substance which could thus be isolated was methyl *r*-diphenylsuccinate.

*Methyl hydrogen r-diphenylsuccinate* separates from hot methyl alcohol, in which it is sparingly soluble, in small pyramids. It dissolves sparingly in boiling benzene, moderately readily in cold ether. It melts at 196—198° after slight previous sintering:

0.3303 neutralised 17.45 c.c. of 0.0666 *N*-alkali. Calc.: 17.47 c.c.

0.1847 gave 0.4878 CO<sub>2</sub> and 0.0948 H<sub>2</sub>O. C=72.0; H=5.7.

C<sub>17</sub>H<sub>16</sub>O<sub>4</sub> requires C=71.8; H=5.7 per cent.

The sodium salt separates from its aqueous solution in small prisms:

0.4456 \* lost 0.0962 at 100—110°. H<sub>2</sub>O=21.6

C<sub>17</sub>H<sub>15</sub>O<sub>4</sub>Na.4H<sub>2</sub>O requires H<sub>2</sub>O=19.05 per cent.

0.1690 † gave 0.0385 Na<sub>2</sub>SO<sub>4</sub>. Na=7.37.

C<sub>17</sub>H<sub>15</sub>O<sub>4</sub>Na requires Na=7.50 per cent.

#### *Action of Aniline on r-Diphenylsuccinic Anhydride.*

A solution of the *r*-anhydride (5 grams) in benzene (10 c.c.) was added to aniline (1.85 grams) dissolved in the same solvent (15 c.c.); in the course of a few seconds, a copious, white precipitate commenced to separate, and the solution speedily became semi-solid. The *r*-diphenylsuccinanilic acid, which was almost quantitatively precipitated, melted at 168—169°, resolidified, and again melted at 226.5—229°. It was crystallised from a small quantity of warm alcohol.

*r-Diphenylsuccinanilic acid* separates from alcohol in short prisms. It is readily soluble in warm alcohol or benzene, in cold ether or acetone, less readily so in carbon tetrachloride or light petroleum. It dissolves sparingly in cold alcohol or benzene. It melts and evolves gas at 173—175°, resolidifies at a slightly higher temperature, and again melts at 227°; the observed values depend somewhat on the rate of heating and the diameter of the tubes used:

0.1853 gave 0.5163 CO<sub>2</sub> and 0.0939 H<sub>2</sub>O. C=76.0; H=5.7.

0.3721 „ 13.6 c.c. N<sub>2</sub> at 16° and 765 mm. N=4.3.

C<sub>22</sub>H<sub>19</sub>O<sub>3</sub>N requires C=76.5; H=5.5; N=4.1 per cent.

#### *Conversion of r-Diphenylsuccinanilic Acid into Diphenylsuccanil.*

A. *By the Action of Heat.*—*r*-Diphenylsuccinanilic acid was gradually heated to 230°, when complete fusion was obtained. The substance solidified, when cooled, to a pale yellow mass which,

\* Air-dried.

† Dried at 190—110°.

after being crystallised from benzene, yielded fine, colourless needles; these were identified as diphenylsuccinanil from the melting point ( $229-230^{\circ}$  after slight shrinkage at  $227^{\circ}$ ) and analysis (Found: C=80.9; H=5.2. Calc.: C=80.7; H=5.2 per cent.). Anschütz and Bendix (*loc. cit.*) describe the substance as separating from benzene in fine, colourless needles which melt at  $226-227^{\circ}$ , from acetic acid in larger, shining needles melting at  $230-231^{\circ}$ .

B. *By the Action of Ethyl-alcoholic Hydrogen Chloride.*—The acid (1.1 grams) was gently warmed with a 3 per cent. solution of hydrogen chloride in ethyl alcohol; it did not immediately dissolve, but, on reaching the boiling point, a copious, crystalline precipitate speedily separated. Boiling was continued during four hours, during which no change in the appearance of the product was observed. The alcohol was removed, and the residue crystallised from benzene, when diphenylsuccinanil (0.7 gram) melting at  $229-230^{\circ}$  was readily obtained.

The behaviour of *r*-diphenylsuccinanilic acid under these conditions is thus similar to that of the anilic acid, melting at  $220^{\circ}$ , described by Anschütz and Bendix.

*Action of p-Toluidine on r-Diphenylsuccinic Anhydride.*

Molecular quantities of *r*-diphenylsuccinic anhydride and of *p*-toluidine were dissolved in benzene and mixed; after a few seconds, the solution became cloudy, and in the course of a few minutes, *r*-diphenylsuccino-*p*-toluidic acid was almost quantitatively precipitated. The crude substance melted and evolved gas at  $194-196^{\circ}$ . It was crystallised from slightly aqueous alcohol.

*r*-Diphenylsuccino-*p*-toluidic acid separates from aqueous alcohol in small needles. It is readily soluble in hot alcohol, sparingly so in hot benzene, and very sparingly so in hot water; it dissolves readily in cold acetone or ether, less readily in cold chloroform. It melts at  $195-196^{\circ}$  and does not appear to suffer decomposition below  $270^{\circ}$ :

0.1613 neutralised 6.8 c.c. of 0.0666 *N*-alkali. Calc.: 6.75 c.c.

0.1850 gave 0.5229  $\text{CO}_2$  and 0.0960  $\text{H}_2\text{O}$ . C=77.1; H=5.8.

0.3842 „ 12.8 c.c.  $\text{N}_2$  at  $18^{\circ}$  and 762 mm. N=3.95.

$\text{C}_{23}\text{H}_{21}\text{O}_3\text{N}$  requires C=76.9; H=5.9; N=3.90 per cent.

At its melting point, *r*-diphenylsuccino-*p*-toluidic acid loses water and passes into the tolii (see later). With slightly impure specimens of the acid, this decomposition is very evident, and water vapour is freely evolved. With the pure acid, however, some external impulse appears requisite to render this effect manifest.

Silver *r*-diphenylsuccino-*p*-toluidate forms a voluminous, white powder:

0.3275 gave 0.0744 Ag. Ag = 22.72.

$C_{23}H_{20}O_3NaAg$  requires Ag = 23.16 per cent.

Methyl *r*-diphenylsuccino-*p*-toluidate was prepared by the action of an excess of methyl iodide on dry silver diphenylsuccino-*p*-toluidate, and was purified by crystallisation from a small quantity of ethyl alcohol, from which it separates in well-defined, microscopic needles melting at 173–174.5°:

0.1395 gave 0.3923  $CO_2$  and 0.0807  $H_2O$ . C = 76.7; H = 6.5.

$C_{24}H_{23}O_3N$  requires C = 77.2; H = 6.2 per cent.

*Conversion of r-Diphenylsuccino-p-toluidic Acid into Diphenylsuccino-p-tolil.*

A. *By the Action of Ethyl-alcoholic Hydrogen Chloride.*—The acid (1.8 grams) was heated under reflux with ethyl-alcoholic hydrogen chloride solution (8 per cent.; 10 c.c.). A homogeneous solution was readily obtained, from which a precipitate separated after a few minutes. The solvent was removed on the water-bath and the residue purified by crystallisation from much alcohol.

*Diphenylsuccino-p-tolil* separates from boiling ethyl alcohol in long, slender needles which, although apparently perfectly stable when dry, frequently crumble to microscopic prisms when preserved beneath the mother liquor. It dissolves sparingly in the boiling, very sparingly in the cold solvent; it is readily soluble in cold acetone, moderately so in cold chloroform or benzene, and sparingly so in cold ether. It melts at 170°:

0.1739 gave 0.5182  $CO_2$  and 0.0884  $H_2O$ . C = 81.3; H = 5.7.

$C_{23}H_{19}O_2N$  requires C = 80.9; H = 5.6 per cent.

B. *By the Action of Heat.*—The *r*-acid was heated in a small tube at 195–205° during fifteen minutes, at the end of which period the evolution of gas had ceased. The residue was crystallised from alcohol, from which it separated in slender needles which disintegrated to microscopic prisms. It melted at 170°, and was thus identified as diphenylsuccino-*p*-tolil.

The behaviour of *r*-diphenylsuccino-*p*-toluidic acid is thus very similar to that of the corresponding anilic acid; it is, however, curious that the melting point of the tolil is lower than that of the toluidic acid, whilst the reverse is the case with the aniline derivatives.

*Action of Alkali on Diphenylsuccino-p-tolil.*

Diphenylsuccino-*p*-tolil (5 grams) was boiled during forty-five minutes with aqueous-alcoholic sodium hydroxide solution (1·2*N*: 40 c.c. Water:alcohol:1:3). The sodium salts thus formed were converted into the barium derivatives, which were separated by treatment with water. From the less readily soluble salt, *r*-diphenylsuccino-*p*-toluidic acid, melting at 194–195°, was easily isolated; the more readily soluble portion yielded, on acidification, crude mesodiphenylsuccino-*p*-toluidic acid, which was purified by crystallisation from slightly diluted acetic acid.

mesoDiphenylsuccino-*p*-toluidic acid separates from alcohol or dilute acetic acid in minute, colourless needles which melt and decompose slightly at 206°. It is moderately soluble in cold methyl or ethyl alcohol or in acetic acid, sparingly so in water or hot benzene, readily so in ether or acetone, and practically insoluble in light petroleum or carbon tetrachloride. When heated at 215° during five minutes or boiled with ethyl-alcoholic hydrogen chloride, it is transformed into diphenylsuccino-*p*-tolil:

0·1216 neutralised 3·4 c.c. of *N*/10-sodium hydroxide. Calc.: 3·39 c.c.

0·1457 gave 0·4128 CO<sub>2</sub> and 0·0804 H<sub>2</sub>O. C=77·25; H=6·13.

C<sub>28</sub>H<sub>21</sub>O<sub>3</sub>N requires C=76·88; H=5·85 per cent.

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## LXXVII.—*The Inflammation of Mixtures of Methane and Air in a Closed Vessel.*

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WHEN an inflammable mixture of gas and air is ignited within an inflexible closed space, flame travels throughout the mixture in a manner and at a speed dependent mainly on the nature and proportion of the inflammable gas present. The manner in which the flame spreads through the mixture is affected also by the shape

of the containing vessel and the position of the point of ignition, and the speed of the flame is affected by these factors as well as by the intensity of the means of ignition and the initial temperature and pressure of the mixture. To such causes of variation in the manner and speed of the spreading of flame must be added mechanical agitation or turbulence of the mixture, such as is induced, for example, within a gas-engine cylinder during the introduction of the charge (see Dugald Clerk, "The working fluid of internal-combustion engines," Gustave Ganet Lecture, Junior Institution of Engineers, 1913).

The inflammation of the mixture within the closed vessel, inasmuch as it results in the formation of products of combustion at a high temperature, causes an increase of pressure. If the vessel were impervious to heat, the maximum pressure developed would afford a measure of the thermal energy of the products of combustion, which should be equal to the chemical energy of the uninflamed mixture.

The present paper records the results of a study of the inflammation of different mixtures of pure methane and air in closed spherical vessels. The principal data obtained were: (1) the maximum pressures developed, (2) the rates of development of pressure, and (3) the speeds of propagation of flame. Details as to the manner in which these data were obtained, and of the precautions taken to ensure their accuracy, are given in the experimental portion of the paper.

#### *Development of Pressure.*

In the table that follows are given the maximum pressures developed by different mixtures of methane and air when ignited within spherical vessels of about (a) 4 litres and (b) 16 litres capacity, 19.5 and 31.2 cm. in diameter, respectively. For comparison, Mallard and Le Chatelier's determinations (*Ann. des Mines*, 1883, [viii], 4, 379), for which they used a cylindrical vessel 17 cm. long and 17 cm. in diameter, are included in the table on p. 842.

These results are shown graphically in Fig. 1. It is of importance to notice that the maximum pressures for similar mixtures in the 4-litre and the 16-litre spheres, as determined by interpolation, are practically identical.

The values quoted as Mallard and Le Chatelier's are their observed values (*loc. cit.*, p. 509). They are rather irregular and are considerably higher than the results obtained for similar mixtures in the spheres. This may be due to impurity of the com-



Methane in mixture. Per cent. by volume.	Maximum recorded pressures above atmospheric. Atmospheres.		
	4-Litre sphere.	16-Litre sphere.	3-86-Litre cylinder (Mallard and Le Chatelier).
6.05	—	2.86	—
6.30	3.20	—	—
6.80	5.10	—	5.51
6.85	—	4.35	—
7.45	5.64	—	—
7.80	—	5.85	—
7.95	6.09	—	—
8.00	—	—	6.53
8.45	6.40	—	—
8.80	—	6.66	—
9.20	6.73	—	7.41
9.40	6.80	—	—
9.50	—	—	7.75
9.65	6.90	—	—
9.80	—	6.94	7.55
10.00	—	—	7.34
10.10	6.97	—	—
10.25	6.97	—	—
10.60	—	—	7.48
10.75	6.87	—	—
10.80	—	6.80	—
11.20	—	—	8.94
11.40	6.73	—	—
11.90	—	6.40	—
12.10	6.36	—	—
12.50	—	—	6.46
12.80	—	5.78	—
12.90	5.78	—	—
13.40	4.80	—	—
13.90	3.54	—	—

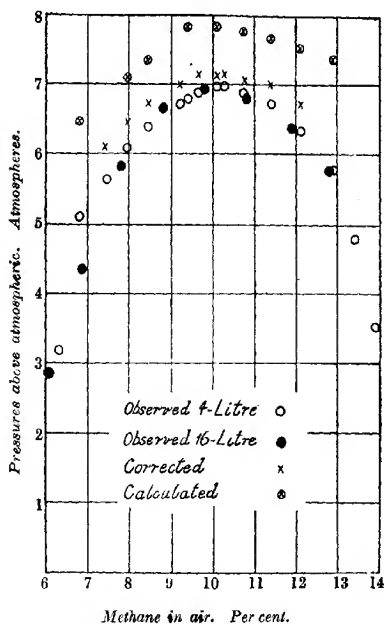
bustible gas used, regarding which the fact is recorded (*loc. cit.*, p. 409) that it contained some gas richer in carbon than methane. The gas was prepared from sodium acetate, and would contain ethylene and acetone vapour.

Reference should be made also to some experiments by Beyling (*Glückauf*, 1906, **42**, 130), who used a cylindrical vessel of 42 litres capacity, 33.5 cm. in diameter and 42.5 cm. long. The maximum pressure recorded as produced by any mixture of methane and air was 6.5 atmospheres. In a vessel of smaller capacity (about 11 litres) the maximum pressure was the same.

By reason of the shape of their explosion-vessel, Mallard and Le Chatelier found it necessary to introduce a correction for cooling during the propagation of flame, averaging about 10 per cent. on their observed pressures. If ignition of an inflammable mixture is exactly at the centre of a perfectly spherical vessel, it is probable that the propagation of flame follows regular concentric spherical surfaces in such a manner that the flame reaches the

walls of the vessel simultaneously at all points; for, except with very slowly moving flames, or, possibly, in very large vessels, it is unlikely that convection currents will have time materially to affect the speed in any particular direction. The whole of the mixture is thus inflamed before cooling by conduction of heat by the walls of the vessel can come into play.\*

FIG 1.



If, however, the vessel is not perfectly spherical, or if ignition is not truly central, flame will touch the walls sooner at some places than at others, and cooling of the products of combustion will begin before propagation of flame is complete. The maximum

\* Cooling by the walls, before the whole mixture is inflamed, may cause a negligible loss of heat if the unburnt mixture in contact with them is heated by compression (due to dilation of the burnt mixture at the centre of the vessel) before flame reaches it.

pressure within the vessel as recorded by a gauge is not then that which the mixture would exert were the whole brought at once to the temperature of combustion. The fact that Mallard and Le Chatelier used a cylinder for their experiments, although they ignited the mixture at the centre, caused the propagation of flame within the vessel to assume two phases. During the first phase the flame travelled from the centre as, presumably, a spherical envelope until it touched the walls of the vessel (the height of which was equal to the diameter). The second phase then began and continued until the flame reached the curve of intersection of the ends with the cylindrical walls, when inflammation was complete. Throughout this second phase, cooling of the products of combustion by the walls took place, the amount of cooling increasing with the progress of the flame, since the area of the surface of the cylinder in contact with the heated gases increased.

A correction to be added to Mallard and Le Chatelier's recorded figures for maximum pressures is, on this reasoning, necessary. The correction when applied brings the pressures developed by all their mixtures of "methane" and air from one to one and a third atmospheres higher than the pressures recorded in the spherical vessels. The question then arises whether a similar correction should not also be applied to the latter results—whether, in fact, one is justified in assuming that with central ignition in a spherical vessel flame spreads at the same speed in all directions. Langen ("Mitteilungen u. Forschungsarbeiten aus dem Gebeite des Ingenieurwesens," vol. 8, 1903), who used a spherical vessel for similar experiments, did, indeed, introduce a "cooling correction." This, however, was on account of a short neck, at the top of the sphere, to which the pressure-gauge was attached; Langen assumed that throughout the spherical portion of his vessel the flame in any given mixture spread in all directions at the same speed.

In order to test the truth of this supposition, a series of measurements was made of the intervals of time that elapsed between ignition and the advent of flame at the top and bottom of a closed vessel filled with different mixtures of methane and air. With all mixtures containing more than 7.5 and less than 12.5 per cent. of methane, the time-intervals for upward and for downward propagation of flame were identical. They coincided also for each mixture with the time that elapsed between ignition and the attainment of maximum pressure in a vessel of the same dimensions. With mixtures containing less than 7.5 and more than 12.5 per cent. of methane, in which the rate of propagation of flame is slow, flame reached the bottom of the vessel later than it reached the top by an amount of time which varied with the methane-con-

tent of the mixture. Thus the measurements for three mixtures were:

Methane in mixture. Per cent.	Time required for the flame to travel 9.75 cm. from the point of ignition.	
	Upwards.	Downwards.
6.40	0.260 sec.	0.468 sec.
8.95	0.169 "	0.234 "
13.00	0.219 "	0.320 "

With such mixtures, therefore, cooling of the products of combustion takes place before the attainment of the maximum recorded pressure, even in a spherical vessel, by reason of the contact of the upper part of the flame with the walls of the vessel before the lower part of the mixture is burnt.

It should be noted that the limits of inflammability of methane-air mixtures ignited at the centre of a closed spherical vessel are 5.6 per cent. lower and 14.8 per cent. upper (T., 1911, 99, 2013). The progress of the flame in these mixtures is sufficiently slow to follow by the eye; the flame travels upwards from the spark as an inverted cone, fills the upper third of the vessel, and thence travels slowly downwards as a horizontal disk to the bottom.

With the mixtures containing more than 7.5 and less than 12.5 per cent. of methane, however, no loss of heat through cooling by the walls before the whole of the mixture has been inflamed should arise in a spherical vessel, other than the negligible quantity transmitted by the layer in contact with the walls during the interval of time that elapses between its compression by the inflamed core (and consequent heating) and its burning. Over this range, then, no such correction for cooling as Mallard and Le Chatelier and Langen applied is required when perfectly spherical vessels are used and ignition is at the centre. One would arrive at the same conclusion from the fact, already noted, that the maximum pressures recorded were the same, within 1 per cent., over the range 7.5 to 12.5 per cent. of methane, in the 4-litre as in the 16-litre sphere, although the ratio surface/volume was 1.6 times as great with the former as with the latter.

Experiment thus shows that one is justified in assuming, over the major portion of the range of inflammable mixtures of methane and air, no loss of heat in a spherical vessel due to contact of part of the flame with the walls before the whole of the mixture is burnt. Yet one cannot assume that the maximum recorded pressure in such a vessel gives a measure of the internal energy of the products of combustion, which should be equal to the chemical energy of the unignited mixture, or, in other words,

that the pressure recorded is that which would be attained were the vessel impervious to heat.

Apart from loss by radiation during the propagation of flame, it must be remembered that at the moment when the vessel is just filled with flame (that is, at the moment of maximum recorded pressure in a spherical vessel), the products of combustion are not in thermal equilibrium (see, in this connexion, the First Report [1910] of the Committee, appointed by the British Association, for the investigation of gaseous explosions). Hopkinson, *Proc. Roy. Soc.*, 1906, [A], 77, 387) has shown that at the moment of maximum pressure of a mixture of coal gas and air, the temperature around the point of ignition at the centre of a cylindrical vessel was several hundred degrees higher than the mean temperature (as deduced from the pressure), owing to adiabatic compression of the products of combustion there during the burning of the remainder of the mixture; whilst at the sides and ends of the vessel, where the gases were compressed before ignition, the temperature reached was as much below the mean.

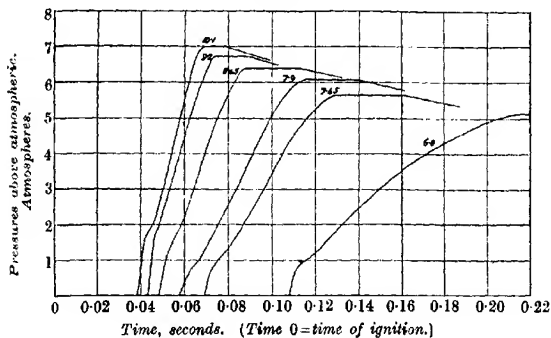
If the volumetric heats of the gases comprising the products of combustion were constant at all temperatures, the attainment of a uniform temperature within a closed vessel by convection and conduction would cause no alteration in pressure; but inasmuch as the volumetric heats are not constant, being perhaps half as great again in the hottest as in the coldest part of the gaseous mass, the attainment of thermal equilibrium should be attended by a change of pressure.

During the time that thermal equilibrium is being established, after complete inflammation has taken place, the cold walls of the spherical containing vessel are everywhere in contact with hot gases, so that simultaneously with any increase in pressure that might result from the equalisation of the temperature differences within the gaseous mass, there is a reduction of pressure due to loss of heat by conduction. This loss, and radiation losses during the same period as well as during the propagation of flame, combine to render the recorded pressures lower than those representative of the chemical energy of the unignited mixtures. It is difficult to make even a rough calculation of the change of pressure that should occur owing to the establishment of thermal equilibrium, because of lack of knowledge of the distribution of temperature within a spherical vessel at the moment of complete inflammation. It is possible, however, if certain assumptions are made, to obtain some idea of the order of magnitude of the pressure change from an examination of the time-pressure diagrams.

Diagrams for representative mixtures used in the 4-litre sphere

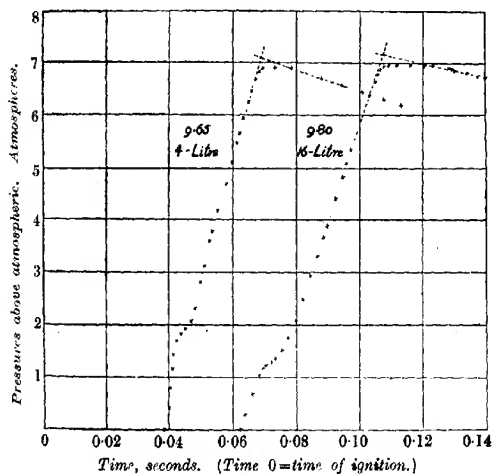
are shown in Fig. 2, whilst in Fig. 3 are given the diagrams for mixtures of nearly the same methane-content, the one (9.65 per

FIG. 2.



cent. methane) in the 4-litre and the other (9.80 per cent. methane) in the 16-litre sphere. These diagrams are reproduced on a

FIG. 3.



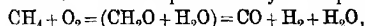
different scale from the actual records of the indicator in the manner described in the experimental portion of this paper.

Examination of these curves shows that each exhibits three stages of development. During the first stage the pressure increases proportionately with the time, during the second it remains constant, and during the third it gradually decreases.

The first stage, during which the pressure increases, corresponds with the propagation of flame within the sphere; as will be shown later, the maximum pressure for all mixtures containing between 7.5 and 12.5 per cent. of methane is attained simultaneously with the advent of flame at the boundary of the mixture. For mixtures containing less than 7.5 or more than 12.5 per cent. of methane, the attainment of maximum pressure synchronises with the advent of flame at the top of the vessel.

The last stage, the beginning only of which is shown in each diagram, represents the cooling of the products of combustion.

The second stage, during which the recorded pressure remains constant, may represent any or all of three possibilities: (1) The occurrence of successive stages in the combustion of methane, the mechanism of which can be represented by the equation



with subsequent burning of the carbon monoxide and hydrogen if oxygen is in excess; (2) exothermic secondary reaction between carbon monoxide and steam (compare Bone, *Phil. Trans.*, 1915, [A], 215, 318); or (3) the equalisation of temperature differences within the gaseous mass, with consequent increase of pressure due to change in the volumetric heats of the products of combustion.

The duration of the period of constant pressure varies with the composition of the mixture of methane and air, the time intervals being:

Methane, per cent.	Duration of period of constant pressure.
7.45	0.031 sec.
7.95	0.026 "
8.45	0.024 "
9.20	0.018 "
9.40	0.010 "
9.65	0.009 "
10.10	0.010 "
10.25	0.009 "
10.75	0.013 "
11.40	0.018 "
12.10	0.024 "

These figures are not consistent with either of the suppositions (1) and (2) given above; for if stages in the combustion of methane are indicated by the period of constant pressure, one would expect that period to be shorter the greater the excess of oxygen present in the mixture, whilst the occurrence of the exothermic secondary reaction between carbon monoxide and steam should be most pro-

nounced when there is excess of methane above that required for complete combustion to carbon dioxide and steam.

On the other hand, the figures support the view that the change of volumetric heats of the gases during the attainment of thermal equilibrium is responsible for an increase of pressure balancing a decrease due to cooling; for the duration of the period of constant pressure is shorter the higher the pressure attained, that is to say, the higher the mean temperature of the products of combustion. Moreover, reference to Fig. 3 shows that the period of constant pressure for mixtures of about the same methane-content was nearly twice as long in the 16-litre as in the 4-litre sphere.

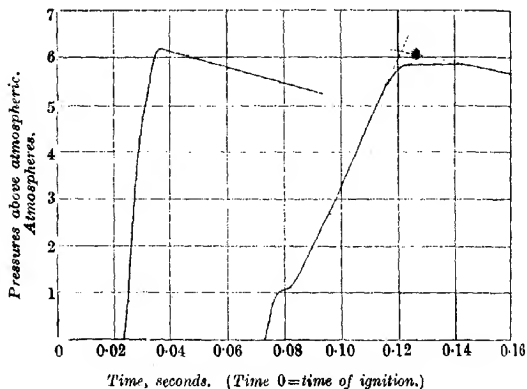
Let us, then, assume that the second stage in the time-pressure diagrams represents a balance between a gradual decrease of pressure that begins as soon as inflammation of the mixture is complete and is due to cooling by the walls of the vessel, and an increase of pressure incident at the same moment and due to the gradual attainment of thermal equilibrium. Mallard and Le Chatelier have shown (*loc. cit.*, p. 454, and Plate XIV, Fig. 8) that the cooling curve for the products of combustion of methane and air is a straight line. It is therefore permissible to extend the cooling curves of the time-pressure diagrams backwards, as shown in Fig. 3. The portion of each curve representing the propagation of flame within the vessel is, after the initial impetus to the flame given by the source of ignition has died down, also nearly a straight line, although there is a slight diminution in the rate of development of pressure just before the maximum is reached. A line drawn extending the straight portion of this curve so as to cut the prolongation of the cooling curve should give, within a close approximation, the pressure that would be attained after the complete inflammation of the mixture did no cooling take place. This has been done for the two curves in Fig. 3, from which it will be seen that the "correction" amounts to, at most, 3 per cent.

The validity of the assumption that such a correction can and should be applied might be tested if means could be employed to ensure a rapid equalisation of the temperature differences within the vessel at the moment of complete inflammation. Experiments made in the course of another investigation (see "Third Report of the Explosions in Mines Committee," p. 26, London, 1913), during which a small fan was rapidly revolved within the sphere, may serve to illustrate the effect of aiding convection currents. The fan had four helical blades and was run at the rate of 100 revolutions per second. The results of a pair of experiments, one with and the other without the fan, using a mixture of ethane and air



containing 4.05 per cent. of ethane, are shown in Fig. 4. The maximum pressure recorded when the fan was revolving was higher than when the mixture was at rest by 0.23 atmosphere, an amount a little more (0.07 atmosphere) than the "correction" obtained in the manner described. This diagram illustrates also the effect of turbulence of the mixture on the speed of inflammation, an effect already noted by Dugald Clerk and Hopkinson. With the fan running, the time taken, measured from the moment of ignition, for the attainment of maximum pressure was 0.0362 sec.; without the fan, it was 0.1244 sec. No doubt the higher pressure reached in the former experiment was in part due to smaller radiation loss during the more rapid propagation of flame.

FIG. 4.



Whatever the cause of evolution of heat, the horizontal portion of the time-pressure diagram represents a balance between heat evolved after flame has travelled throughout the mixture and heat dissipated, and the correction to be applied on this score cannot exceed the quantity deduced by extrapolation of the cooling and propagation curves. In Fig. 1 are shown the "corrected" pressures for mixtures over the range 7.5 to 12.5 per cent. of methane, together with the calculated maximum pressures those mixtures should produce, taking Langen's values for the specific heats of the various gases and assuming no loss of heat by radiation.

The calculated values are about 10 per cent. greater than the observed over the whole range. This difference, assuming the

correctness of the values taken for the specific heats of the gases, must be due mainly to loss of heat by radiation during the propagation of flame in the spheres, for it has been shown that up to the time of attainment of maximum pressure flame does not touch the walls of the vessels.\* For information regarding the probable loss of heat by radiation, only the results of Hopkinson (*Proc. Roy. Soc.*, 1911, [A], **84**, 155) with mixtures of coal-gas and air, and of David (*Phil. Trans.*, 1912, [A], **211**, 375) with coal-gas-air and hydrogen-air mixtures are available, and direct comparison of these with methane-air mixtures cannot be made.

It has been shown, however (David), that up to the time of maximum pressure (attained in 0.05 sec.), a 15 per cent. coal-gas-air mixture radiated about 3 per cent. of its total heat of combustion, the maximum temperature reached being 2400° abs. A 25.4 per cent. hydrogen-air mixture, which developed the same maximum temperature, radiated about 0.5 per cent. only of its total heat of combustion up to the time of attainment of maximum pressure (in 0.017 sec.). The coal-gas used probably contained about 50 per cent. of hydrogen and 35 per cent. of methane (and other hydrocarbons); it is known that the radiation from the mixtures is due almost entirely to the steam and carbon dioxide that they contain, and that carbon dioxide has a radiating power about 2.4 times that of an equal volume of steam (R. von Helmholtz, "Die Licht- und Wärmestrahlungverbrennender Gase," Berlin, 1890); an estimated loss due to radiation of about 10 per cent. of the total heat of combustion during the propagation of flame in the mixtures of methane and air may therefore be not far from the truth.

#### *Propagation of Flame.*

Each of the time-pressure diagrams shown in Figs. 2 to 4 has been plotted with the time of passage of the secondary discharge that caused the ignition of the mixture as zero time. It has been assumed by the majority of experimenters on the inflammation of gaseous mixtures in closed vessels that the time of ignition synchronises with the time of first manifestation of pressure on the indicator or gauge. Baird and Alexander (*Proc. Roy. Soc.*, 1905, [A], **76**, 340) found, however, that this was not so in their experiments with mixtures of coal-gas and air; and it is apparent from the diagrams for methane-air mixtures given in this paper that there is a definite interval of time, the length of which depends on the composition of the mixture, between the ignition

\* A slight amount of cooling no doubt arises through conduction of heat by the electrodes.

of the mixture at the centre of a spherical vessel and the first appearance of pressure on an indicator fixed at the top.

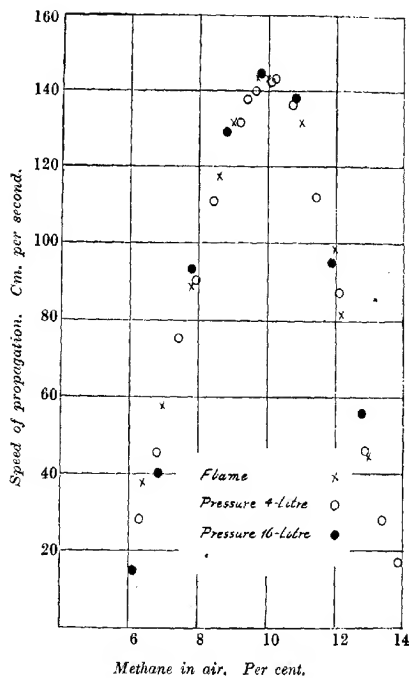
In order to be able to trace the progress of the flame within the vessels from the time-pressure diagrams, records were taken of the time that elapsed between the passage of an electric spark at the centre of a closed vessel containing different mixtures of methane and air and the appearance of flame at a point 7.5 cm. vertically upwards, in the manner described in the experimental portion of this paper. The time-intervals calculated for a distance of 9.75 cm. were found to correspond closely with the times taken for the development of the maximum pressures in similar mixtures in the 4-litre sphere (radius, 9.75 cm.), as the following table

Methane in mixture. Per cent.	Time taken for flame to travel 9.75 cm. upwards. Seconds.	4-Litre sphere.		16-Litre sphere.		Mean speed of flame. Cm. per sec.
		Time between ignition and first appear- ance of pressure. Seconds.	Time between ignition and attain- ment of maximum pressure. Seconds.	Time between ignition and first appear- ance of pressure. Seconds.	Time between ignition and attain- ment of maximum pressure. Seconds.	
6.05	—	—	—	0.4233	1.0370	16
6.30	—	—	0.1800	—	—	28
6.40	0.260	—	—	—	—	37.5
6.80	—	0.1080	0.2150	—	—	45.5
6.85	—	—	—	0.1830	0.3877	40
6.95	0.169	—	—	—	—	58
7.45	—	0.0690	0.1302	—	—	75
7.80	0.110	—	—	0.1021	0.1680	82, 93
7.95	—	0.0574	0.1084	—	—	90
8.45	—	0.0484	0.0878	—	—	111
8.60	0.083	—	—	—	—	117.5
8.80	—	—	—	0.0713	0.1206	129
9.00	0.074	—	—	—	—	132
9.20	—	0.0428	0.0720	—	—	132
9.40	—	0.0392	0.0707	—	—	138
9.65	—	0.0382	0.0696	—	—	140
9.70	0.068	—	—	—	—	143.5
9.80	—	—	—	0.0623	0.1080	144.5
10.00	0.068	—	—	—	—	143.5
10.10	—	0.0383	0.0684	—	—	142.5
10.25	—	0.0382	0.0682	—	—	143
10.75	—	0.0395	0.0715	—	—	136
10.80	—	—	—	0.0665	0.1130	138
11.00	0.074	—	—	—	—	132
11.40	—	0.0498	0.0870	—	—	112
11.90	—	—	—	0.1000	0.1640	95
12.00	0.099	—	—	—	—	98.5
12.10	—	0.0694	0.1184	—	—	87
12.20	0.120	—	—	—	—	81
12.80	—	—	—	0.1320	0.2800	56
12.90	—	0.1150	0.2120	—	—	46
13.00	0.219	—	—	—	—	44.5
13.40	—	0.1600	0.3470	—	—	28
13.90	—	0.2160	0.6700	—	—	17

shows. In the same table are given the time-intervals between ignition and the attainment of maximum pressure in the 16-litre sphere (radius, 15.6 cm.) and the calculated mean speeds of the flames in cm. per second.

The correspondence between the time taken for flame to travel from the centre to the top in the spheres and the time taken for

FIG. 5.



the attainment of the maximum pressures is perhaps best shown in Fig. 5, where the mean speeds of the flames, in cm. per sec., are plotted against percentages of methane in the mixtures, different symbols being used according as the points on the curve are (1) actual determinations of the rate of travel of flame, (2) calculated from the time-interval between ignition and the attainment of maximum pressure in the 4-litre sphere, or (3) calculated from the time-interval between ignition and the attainment of maximum pressure in the 16-litre sphere.

lated from the time-interval between ignition and the attainment of maximum pressure in the 16-litre sphere.

It is of interest to compare these speeds with the speeds during the "uniform movement" of flame in similar mixtures (see T., 1917, 111, 1044), although the conditions under which propagation takes place are different. The shapes of the speed-percentage curves for the two modes of propagation are similar, the speeds in each exhibiting maxima over the range 9.5 to 10.5 per cent. methane and decreasing regularly on either side of this range. The speeds are, moreover, of the same order of magnitude (compare, for example, the speeds during the uniform movement of flame in a tube 30.5 cm. in diameter), in which connexion it may be noted that the high speeds recorded by Mallard and Le Chatelier for the propagation of flame in mixtures of methane and air in a closed cylinder (*loc. cit.*, p. 464) are due to those authors regarding the first indications of pressure on their time-pressure diagrams as coincident with the times of ignition of the mixtures.

If it is assumed, for the sake of calculation, that the flames in the spheres travelled at the observed mean speeds from the point of ignition, it is found that in the 4-litre sphere no pressure was indicated until the flame had travelled from 5 to 5.5 cm. (the calculated distance is remarkably constant over the whole range of mixtures), whilst in the 16-litre sphere flame travelled from 9 to 10 cm. before any pressure was indicated. That is to say, over the range 7.5 to 12.5 per cent. of methane, where the flame is propagated in all directions at the same speed, about one-fifth of the mixture had been inflamed in each vessel before any indication of pressure was obtained.

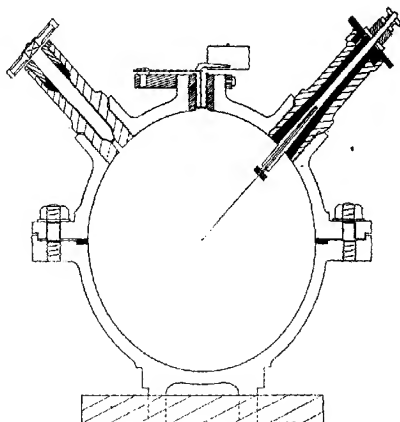
#### EXPERIMENTAL.

*The Measurement of Pressure.*—The spheres, 19.5 and 31.2 cm. in diameter respectively, were machined castings of bronze. A section of one of them—both were of the same design—is shown in Fig. 6. The sphere is cast in two halves bolted together with a loose ring of copper as washer. It is pierced at the top by a hole carrying a fixed sleeve of hardened steel, highly polished, the internal diameter of which is 12.75 mm. A hollow piston of hardened steel is ground and polished to fit the sleeve; the surface of the piston on which the pressure within the vessel acts is 785 sq. mm., the piston being prevented from passing through the sleeve by a thin ring of steel at the base thereof. Other fittings are: (a) a valve for exhaustion and the introduction of the inflammable mixture, (b) insulated electrodes reaching to the centre,

(c) a small window of quartz, and (d) a removable shaft carrying a small broad-bladed fan. The last-named was removed during all the experiments described in this paper, save the one wherein the use of the fan is specified. The fittings on the sphere for the piston, valve, and quartz window are flush with the inner surface, which is highly polished. Both spheres were made by Mr. C. W. Cook, of the University Engineering Works, Manchester.

The manometer is a triangular plate of tempered steel 2.6 mm. in thickness, the base of which is clamped, the apex making contact with the hollow piston in the sphere by means of a loose rod of steel, the lower end of which rests in a conical depression at the

Fig. 6.



centre of the base of the piston, whilst the upper end rests in a similar depression in the spring. A thin strip of steel is attached to the apex of the spring and carries a scribing style, which rests lightly against the surface of a smoked paper band on a drum revolved by an electric motor.

With this form of spring, the maximum strain is the same at all cross-sections, and the inertia is small, since it is the narrow part of the spring which moves most and the wide part least. The deflexion of the scribing style, equivalent to a pressure of one atmosphere, applied to the piston is 1.38 mm. The period of the indicator is  $1/250$ -sec.

The graphs produced by the scribing style on the smoked-paper chart (which receives also a record of the time of passage of the secondary discharge spark used to ignite the mixtures and the trace of an electrically driven tuning-fork making fifty vibrations per second) are measured, after fixation of the chart in a bath of weak spirit varnish, by the aid of a specially designed apparatus (see "Record of First Series of the British Coal Dust Experiments," p. 75, London, 1910), consisting essentially of a microscope with fine cross-wires in the eyepiece and a drum mounted on V-supports in which it can rotate or slide laterally. The circumference of the drum is divided into millimetres and rests against a vernier, whilst lateral movement of the drum is measured by means of a micrometer screw with a divided head.

*Method of Conducting an Experiment.*—The sphere having been assembled, it was exhausted of air to within a few mm. of mercury by means of a Gaede mercury pump, and the mixture to be experimented with introduced. Each mixture was prepared in an 18-litre glass gas-holder over glycerol and water, well shaken, and allowed to remain during six hours, and analysed before use. The secondary discharge used to ignite the mixtures was obtained from a "10-inch" X-ray coil by breaking a current of 10 amperes in the primary circuit, the trembler being locked. The discharge passed across a 10 mm. gap at the centre of the sphere, and simultaneously a record of its passage was made on the smoked-paper chart on the revolving drum.

*Speed of Propagation of Flame.*—Measurements of the speeds of propagation of flame were obtained for a series of mixtures by recording the time of passage of the secondary discharge used to ignite them at the centre of the vessel and the time at which short screen wires of copper 0.025 mm. in diameter, stretched at a distance of 7.5 cm. vertically above and below the point of ignition, were melted. The screen wires carried an electric current of 0.5 ampere at 4 volts and were in series with the electromagnets of delicate Deprez indicators, the latency or "time-lag" of which was found to be negligible. (The armatures, carrying aluminium styles for recording on the smoked-paper chart, moved freely with a current of 0.1 ampere at 1 volt.)

*Calculation of Theoretical Maximum Pressures.*—For the purpose of calculating the theoretical maximum pressures that should be given by the different mixtures, it was necessary to obtain information as to the proportion of the methane completely burned to form carbon dioxide and steam at the time of attainment of maximum pressure, more particularly in those mixtures containing excess of methane. To this end, a series of experiments was made

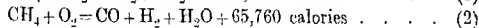
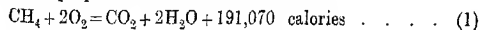
in which a capillary tube of copper, fitted with a tap, was fixed through the side of the 4-litre sphere (in place of the quartz window). The tube projected 4.8 cm. within the sphere (that is, midway between the centre and the circumference), and outside the sphere, beyond the tap, it was bent so as to dip below the surface of mercury in a trough. A gas-collecting tube of 25 c.c. capacity, filled with mercury, was inverted in the trough over the end of the bent tube.

The sphere was filled with the inflammable mixture in the usual manner, enough gas passed through the copper delivery tube to displace the air therein, and the tap closed. The mixture having been ignited, the tap was opened at the moment of attainment of maximum pressure by revolving it rapidly through 180 degrees. During the short time that the tap was thus opened, the pressure within the sphere forced out into the collecting tube between 5 and 10 c.c. of the products of combustion, a quantity sufficient for accurate analysis.

The results of the analyses, after making a correction for the unburnt mixture contained in the capillary tube, were as follow:

Methane in original mixture. Per cent.	Analysis of products of combustion.				
	CO <sub>2</sub> .	O <sub>2</sub> .	CO.	H <sub>2</sub> .	CH <sub>4</sub> .
7.90	9.25	3.82	0.15	nil	nil
9.40	11.14	0.74	0.26	nil	nil
9.90	10.66	0.13	1.12	0.40	0.24
10.00	10.86	0.04	1.08	0.68	0.04
10.70	9.04	nil	3.63	2.21	0.10
11.05	9.00	nil	3.44	1.95	0.23
12.10	8.09	0.07	5.85	4.00	0.07
12.90	6.08	0.05	7.78	6.73	0.36
13.90	5.45	nil	8.95	9.45	1.00
14.70	4.13	nil	9.85	11.15	0.61

These results should be compared with similar analyses of "flame gases" obtained during the propagation of flame in upper limit mixtures with air and with mixtures of oxygen and nitrogen containing less oxygen than air (T., 1914, 105, 2596). The percentages of the total methane in the original mixtures burnt to form carbon dioxide and steam are plotted against the ratios O<sub>2</sub>/CH<sub>4</sub> in the original mixtures in Fig. 7, which includes also the results obtained with the upper limit mixtures. From the curve so obtained, it is possible to estimate for any mixture of methane and air, with sufficient accuracy for the calculation of the heat developed, the proportions in which the reactions:



can be assumed to have taken place during combustion.



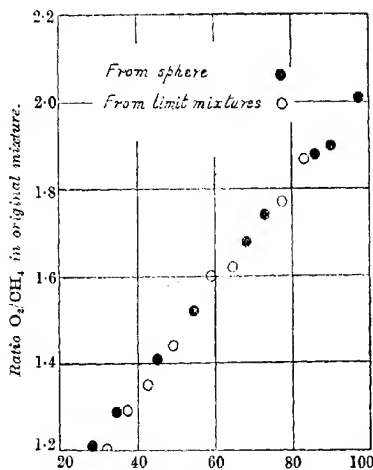
The calculation is as follows. The mixtures being saturated with water vapour at  $15^\circ$ , the original pressure of the mixture is 0.983 atmosphere, with 0.017 atmosphere of water vapour. The final pressure, if the gases are cooled to  $15^\circ$  without condensation of steam, is equal to the original pressure plus the partial pressure of any methane burnt according to equation (2).

Let  $Q$  be the heat of the reaction, then

$$Q = p\text{CH}_4(ag + bq'),$$

where  $p\text{CH}_4$  is the partial pressure of the methane burnt (corrected

FIG. 7.



Percentage of methane burnt appearing as  $\text{CO}_2$  and steam.

for the presence of water vapour),  $a$  and  $b$  represent the proportions burnt according to equations (1) and (2) respectively, and  $q$  and  $q'$  the corresponding heats of combustion.

The rise of temperature,  $t$ , is given by the equation

$$t = \frac{p\text{CH}_4(ag + bq')}{(p\text{H}_2 + p\text{O}_2 + p\text{N}_2 + p\text{CO})(4.8 + 0.00066) + p\text{CO}_2(6.7 + 0.00264) + p\text{H}_2\text{O}(5.9 + 0.00215)}$$

Where unburnt methane remains in the mixture a term for the specific heat of methane, appropriate to the temperature, requires to be introduced in the denominator on the right-hand side of the equation.

The absolute pressure,  $P$ , is given, in atmospheres, by the equation

$$P = \frac{t + 288}{288} (p + p_{\text{CH}_4} \cdot b).$$

The majority of the experiments described in this paper were carried out during the winter of 1912 with the assistance of Mr. M. J. Burgess. For the experiments on the speeds of propagation of flame, as well as for assistance in checking some of the earlier results, I am indebted to Mr. W. Mason.

ESKMEALS,  
CUMBERLAND.

[Received, August 12th, 1918.]

### LXXVIII.—A Synthesis of isoBrazilein and Certain Related Anhydropyranol Salts. Part I.\*

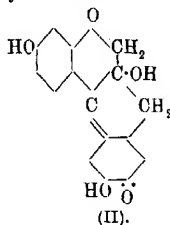
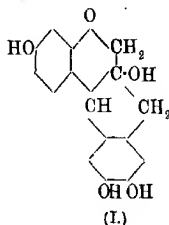
By HERBERT GRACE CHABTREE and ROBERT ROBINSON.

ALTHOUGH accumulated evidence decisively establishes the constitution of brazilin, it must be admitted that the necessary arguments are somewhat intricate, and consequently the problem of the synthesis † of the substance and its more important derivatives

\* The original intention of the authors to publish this research as a single communication has been revised in view of the very considerable delay which has been caused by their inability to complete the experimental work under existing conditions. They have reserved for Part II, a description of the homologues of the methylated isobrazilein salts, and also the intermediate product in the synthesis and the identification of the synthesised isobrazilein with that obtained from brazilin. It is hoped that the method of synthesis of isobrazilein may prove applicable also to the synthesis of isoharmatein.

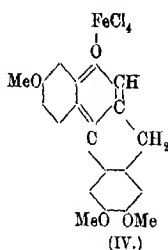
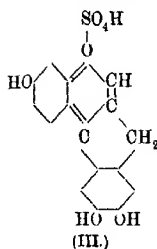
† Pfeiffer and Grimmer in a communication (*Ber.*, 1917, 50, 911) bearing the rather misleading title, "The Brazilin Question," have announced their intention of attacking the problem of the synthesis of brazilin and its derivatives, but are apparently unaware that the method they propose to employ has already been indicated by Perkin and Robinson (*P.*, 1912, 28, 7). The former authors have so far obtained 3-anisylidene-7-methoxy-2:3-dihydro-1:4-benzopyrone, whereas the latter prepared a nearer relative of brazilin, namely, 3-veratrylidene-7-methoxy-2:3-dihydro-1:4-benzopyrone, and stated that they had made observations indicating the probability that the substance could be converted into a derivative of brazilin. This veratrylidene compound was later prepared in larger amount and in a purer condition, and the research was elaborated in various directions, although a number of circumstances have combined to retard the completion of the work. There has, however, never been any intention of abandoning a line of investigation which has always been regarded as likely to lead to a synthesis of trimethylbrazilin.—W.H.P., R.R.

retains considerable interest. Perkin and Robinson (T., 1908, **93**, 515) have already synthesised brazilinic acid and the lactone of dihydrobrazilinic acid, substances containing all the carbon atoms of brazilin, but in which the chromane and hydrindene rings are ruptured as the result of oxidation. Up to the present, no brazilin derivative has been synthesised that contains the characteristic fused ring system of the parent compound, nor does this skeleton occur in the molecule of any substance not itself obtained from brazilin or hæmatoxylin. We are now able to describe a simple method of synthesis of the *isobrazilein* salts, a result which harmonises with previous work and confirms the correctness of the view that brazilin is to be represented by the formula I.

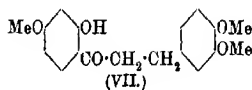
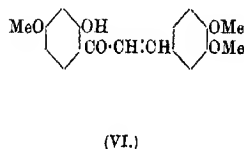
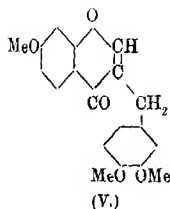


As is well known, brazilin,  $C_{16}H_{14}O_5$ , is converted by oxidation into the quinone brazilein,  $C_{16}H_{12}O_5$  (II), and the latter was found by Hummel and A. G. Perkin (T., 1882, **41**, 367) to be transformed by mineral acids into a series of bright, orange-red salts which were called the *isobrazilein* salts. *isobrazilein* hydrogen sulphate has the composition  $C_{16}H_{11}O_4 \cdot HSO_4$ . Subsequently, these derivatives were examined by Engels, Perkin, and Robinson (T., 1908, **93**, 1121), who devised methods for the preparation of the methyl ethers of the salts and recognised the relation of the series to the anhydropyranol or pyrrylium oxonium salts. The constitutional formulæ III and IV were assigned to *isobrazilein* hydrogen sulphate and to the trimethyl ether of *isobrazilein* ferrichloride\* respectively (*loc. cit.*).

\* Engels, Perkin, and Robinson (*loc. cit.*) did not give names to these ethers which could be used to show their relation to brazilin. The difficulty is that *isobrazilein*, which is really *anhydrobrazilein* and a quinone, contains only two hydroxyl groups and can yield only a dimethyl ether. The formation of a salt produces a further hydroxyl group from the quinonoid oxygen above, and it is possible to have a trimethyl ether of the salts. For this reason it is necessary to speak of *isobrazilein* ferrichloride trimethyl ether, and not of, what at first sight appears more natural, trimethyl*isobrazilein* ferrichloride. The systematic names are very cumbersome, the salt in question being 4:7:5'-trimethoxy-4:3-indeno-1:4-benzopyranol anhydroferrichloride.

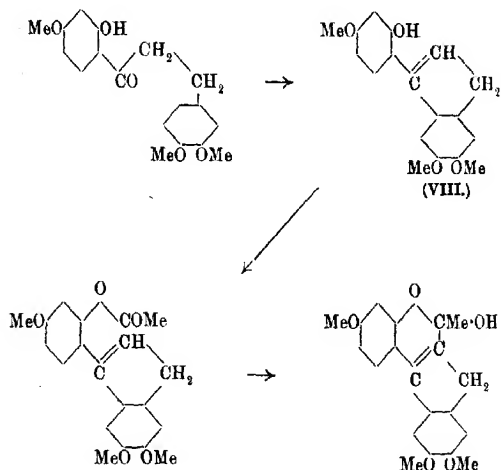


Now, these particular derivatives of brazilin were obviously suitable objects of a synthetical investigation, partly on account of the vivid fluorescence which they exhibit under appropriate conditions, rendering the formation of a mere trace detectable, and also because the pyrrylium nucleus may be produced by the application of widely differing methods. We thought it very probable that the chromone derivative, V, would be converted into the trimethyl ether of an *isobrazilein* salt by the condensing action of acidic dehydrating agents, and our first attempts were accordingly directed towards the preparation of this substance by a method similar to that which had been employed for the synthesis of another 3-substituted chromone, namely, anhydrobrazileic acid (Perkin and Robinson, T., 1908, **93**, 504). Butein trimethyl ether (VI) (A. G. Perkin and Hummel, T., 1904, **85**, 1468) was obtained by the condensation of paeanol and veratraldehyde and reduced by the catalytic method to its dihydro-derivative (VII), but all attempts to convert this substance into a pyrone by condensation with ethyl formate or ethyl oxalate by means of sodium or analogous agents were unsuccessful. It was observed, however, that the ketone, VII, exhibited a tendency to produce highly



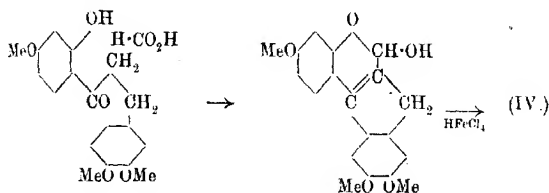
fluorescent substances when heated with acid anhydrides, and by boiling acetic anhydride in the presence of zinc chloride it was completely converted into an oxonium salt isolable in the form of its ferrichloride, and this product closely resembled the braziliin derivative, IV, especially in regard to the characteristic uranium-green fluorescence of its dilute aqueous solution.

The conclusion that the substance is a homologue of *isobrazilein* ferrichloride trimethyl ether was supported by analytical data, and a whole series of similar salts may be obtained by replacing the acetic anhydride by other anhydrides. The synthesis probably occurs as represented below, but it is impossible to decide without further evidence whether indene-ring formation or acetylation is the first stage in the process. The final product indicated is an  $\alpha$ -pyranol, which is converted by the action of acids into an *anhydro*-salt containing the pyrrylium nucleus. In this connexion we have included on p. 874 an account of some experiments made in 1909 by Mr. M. R. Turner, in collaboration with one of us, which go to show that an identical salt is obtained by the action of acid on corresponding  $\alpha$ - and  $\gamma$ -pyrands.



The action of dry hydrogen chloride, together with acetic anhydride and zinc chloride, on dihydrobutein trimethyl ether in the cold furnished a substance which is probably the indene derivative (VIII), and this is converted by the further action of hot

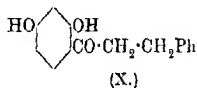
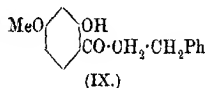
acetic anhydride and zinc chloride into the oxonium salt. The description of the foregoing compounds is reserved for a future communication. It was evident that in order to synthesise an *isobrazilein* salt, it would be necessary to introduce formic acid instead of acetic or other carboxylic acid in these reactions, and many attempts were made to utilise the mixed anhydride of formic and acetic acids in the hope that the phenol, VII, could be formylated and then further condensed in the desired direction. Unfortunately, this mixed anhydride, in the presence of salts such as zinc chloride or sodium acetate, or of acids or tertiary bases, decomposes too readily into carbon monoxide and acetic acid to be of great service as a reagent, and no progress was made along these lines. After numerous experiments in other directions, it was found that prolonged boiling of dihydrobutein trimethyl ether with a large excess of absolute formic acid and zinc chloride gave rise to a product from which *isobrazilein* ferrichloride trimethyl ether could be readily isolated. The synthesis is represented below:



On heating the trimethyl ether salt\* with hydrochloric acid at 150° in a sealed tube, a product was obtained which had all the reactions of *isobrazilein* hydrochloride. This demethylation will be further investigated if possible. The favourable issue of the research depended very largely on the devising of practical methods for the synthesis of hydrochalkone derivatives, and as a preliminary the processes available for the preparation of 2-hydroxy-4-methoxyphenyl phenylethyl ketone (IX) were compared. Beggolini and Marantonio (*Gazzetta*, 1908, **38**, ii, 514) obtained the corresponding dihydric phenol, 2:4-dihydroxyphenyl phenylethyl ketone (X), by the condensation of  $\beta$ -phenylpropionic acid with resorcinol by means of zinc chloride at 140–150°, and gave

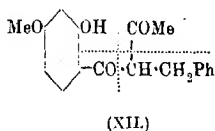
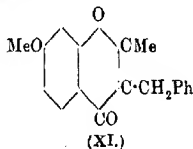
\* Before carrying out the demethylation, the ferric chloride was removed from the substance by conversion through the sparingly soluble orange-red sulphate into the hydrochloride. The sulphate was obtained by gently warming the ferrichloride with concentrated sulphuric acid and pouring into water. The process was repeated, and the hydrochloride obtained from the sulphate by the action of aqueous-alcoholic hydrochloric acid.

conditions under which it was claimed that it could be converted into either a monomethyl ether melting at 74—75° or a dimethyl ether melting at 103—104°.



As the result of our experiments, we are forced to the conclusion that the monomethyl ether melting at 74—75° does not exist, and that the so-called dimethyl ether is really the monomethyl ether. This substance crystallises from alcohol in needles melting at 105°; it contains only one methoxyl group, and may be obtained either by the methylation of the ketone, X, or by the reduction of benzylidenepaeanol. Its alcoholic solution gives a reddish-violet coloration with ferric chloride, but the phenolic function is weak, and the sodium salt is hydrolysed by water to such an extent that the substance may be completely extracted by ether from a suspension in aqueous sodium hydroxide. By far the best general method for the preparation of the hydrochalkone derivatives was found to be the reduction of the unsaturated ketones by hydrogen in the presence of a palladium sol or of palladium-black, and relatively small amounts of the catalyst were found to suffice. Benzylidenepaeanol could be reduced in alcoholic or ethereal solution, but veratrylidenepaeanol (butein trimethyl ether) was not reduced in those solvents even in ethyl acetate. It was, however, readily attacked in acetic acid solution. In the course of preliminary experiments we obtained one substance constituted similarly to the chromone, V. Kostanecki and Różycki (*Ber.*, 1901, **34**, 102) have shown that the acetylation of resacetophenone and of paeanol under correct conditions leads to the formation of chromone derivatives, and we have found that this reaction can be imitated in the case of benzylresacetophenone (X), but not with benzylpaeanol (IX). Acetic anhydride and sodium acetate at the boiling point of the mixture converts the former substance into the acetyl derivative of a hydroxybenzylmethylchromone, which is itself obtained on hydrolysis of the acetyl derivative, and may be converted in the usual manner into a methyl ether. The methyl ether is 7-methoxy-3-benzyl-2-methyl-1:4-benzopyrone (XI), as is proved by the fact that on hydrolysis by means of methyl-alcoholic potassium hydroxide it yields 2-hydroxy-4-methoxyphenyl phenylethyl ketone (IX), benzylacetone, and 2-hydroxy-4-methoxybenzoic acid. The formation of these substances is explicable as the result of the scission of the

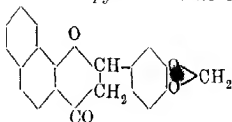
primary product of hydrolysis (XII) in the two directions indicated by the dotted lines.



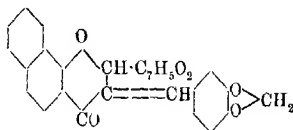
This chromone could not be converted into a salt of *isobrazilein* type, but many examples could be quoted to show that such an observation cannot safely be applied as a criterion of the probable behaviour of a corresponding veratryl derivative. The method which in this case was successfully used in the preparation of a 3-benzylchromone failed in the veratric series, because the condensation of resorcinol and 3:4-dimethoxyphenylpropionic acid in the presence of zinc chloride gave only tarry products.

#### EXPERIMENTAL.

*3':4'-Methylenedioxy-2-phenyl-2:3-dihydro-1:4-α-naphthopyrone and its 3-Piperonylidene Derivative.*



and



It has been pointed out on p. 861 that efforts were made to prepare 3-homoveratrylchromones, and among the possible methods seemed to be that depending on the realisation of the transference of a double bond in a veratrylidenechromanone from the *exocyclic* to the *endocyclic* position. As a preliminary case, the readily accessible substances figured above were prepared, but it was not found possible to convert the piperonylidene derivative into a true chromone by inducing a movement of the ethylene linking. Under varied treatment, the substance remained unchanged or suffered decomposition in other directions. The starting point in these experiments was 1-hydroxy-β-naphthyl methyl ketone



(2-acetyl-1-naphthol), and this was obtained by a slight modification of Friedländer's process (*Ber.*, 1895, **28**, 1946). An intimate mixture of  $\alpha$ -naphthol (50 grams), acetic acid (75 grams), and zinc chloride (75 grams) was heated during thirty minutes at 160–170°. The precipitate obtained by the addition of water to the cooled mass was collected and washed with dilute hydrochloric acid, then dried, and crystallised from methyl alcohol. Three crystallisations gave a product melting at 99° (the pure substance melts at 103°), and this was sufficiently pure for most experiments. Our yield was always much diminished when we adopted the method of purification through the sodium salt, as recommended by Friedländer. Piperonylidene-methyl 1-hydroxy- $\beta$ -naphthyl ketone (Kostanecki, *Ber.*, 1898, **31**, 707) was converted into the corresponding flavanone by a method similar to that frequently employed by Kostanecki and his co-workers. The unsaturated ketone (10 grams) was dissolved in hot alcohol (600 c.c.), and after the addition of concentrated hydrochloric acid (80 c.c.) and water (240 c.c.), the mixture was boiled under reflux during twenty-four hours. The solution was filtered hot, and, on cooling, the flavanone separated in pale orange needles, which were recrystallised from alcoholic hydrochloric acid, and then again twice from alcohol, when they were colourless and melted at 145°:

0.2460 gave 0.6792 CO<sub>2</sub> and 0.0974 H<sub>2</sub>O. C=75.3; H=4.4.

C<sub>20</sub>H<sub>14</sub>O<sub>4</sub> requires C=75.5; H=4.4 per cent.

The substance is sparingly soluble in light petroleum, moderately so in methyl or ethyl alcohol, and dissolves freely in benzene, chloroform, acetone, or ethyl acetate.

*Piperonylidene Derivative.*—Owing to the ease with which the flavanone is reconverted by sodium hydroxide into the unsaturated ketone, it was necessary to employ an acid as the condensing agent in preparing this substance. The flavanone (2 grams) and piperonal (2 grams) were together dissolved in acetic acid (10 grams), and the solution was then saturated with hydrogen chloride. After allowing to remain overnight, the crystals which had separated were collected and crystallised from a mixture of nitrobenzene and alcohol. The substance was so obtained in rich golden balls of needles melting at 206°, and very sparingly soluble in most organic solvents:

0.1986 gave 0.5425 CO<sub>2</sub> and 0.0751 H<sub>2</sub>O. C=74.5; H=4.2.

C<sub>25</sub>H<sub>18</sub>O<sub>6</sub> requires C=74.7; H=4.0 per cent.

The solution of this compound in sulphuric acid is intensely reddish-purple. The nature of the dark green products obtained

by the action of vigorous acid condensing agents, such as phosphoryl chloride, could not be ascertained.

*7-Hydroxy-3-benzyl-2-methyl-1:4-benzopyrone.*

The acetyl derivative (see below) was boiled during two and a-half hours with an excess of dilute aqueous sodium carbonate, when it gradually dissolved as the result of hydrolysis. On cooling, the resulting phenol crystallised, and was collected and recrystallised from alcohol, being obtained in bundles of colourless, silky, prismatic needles melting at  $282^{\circ}$ :

0.1865 gave 0.5217  $\text{CO}_2$  and 0.0906  $\text{H}_2\text{O}$ .  $\text{C}=76.3$ ;  $\text{H}=5.4$ .

$\text{C}_{17}\text{H}_{14}\text{O}_3$  requires  $\text{C}=76.6$ ;  $\text{H}=5.3$  per cent.

The colourless solutions of the substance in cold aqueous sodium hydroxide or hot aqueous sodium carbonate exhibited violet fluorescence, and a similar appearance was obtained when the non-fluorescent solution in cold sulphuric acid was gently heated.

*Acetyl Derivative.*—2:4-Dihydroxyphenyl phenylethyl ketone (10 grams) was mixed with fused sodium acetate (15 grams) and acetic anhydride (20 grams), and heated in an oil-bath at  $170^{\circ}$  during four hours. Water and dilute hydrochloric acid were added to the cooled mass, and when the separated solid was free from acetic anhydride, it was collected, washed, dried, and crystallised from methyl alcohol, from which the compound separated in long, colourless needles melting at  $121^{\circ}$ :

0.2016 gave 0.5473  $\text{CO}_2$  and 0.0998  $\text{H}_2\text{O}$ .  $\text{C}=74.0$ ;  $\text{H}=5.5$ .

$\text{C}_{19}\text{H}_{16}\text{O}_4$  requires  $\text{C}=74.0$ ;  $\text{H}=5.2$  per cent.

The substance was not changed by dilute aqueous sodium hydroxide, and dissolved in sulphuric acid to a very pale yellow solution, which exhibited violet fluorescence on being heated.

*Methyl Ether (XI).*—7-Hydroxy-3-benzyl-2-methyl-1:4-benzopyrone (2 grams) was dissolved in hot methyl alcohol and mixed with methyl sulphate (5 c.c.). The solution was boiled under reflux, and aqueous potassium hydroxide (10 c.c. of 40 per cent.) gradually added during five minutes. The methyl ether was precipitated by the addition of water, but was not obtained in a satisfactory condition, and was therefore dissolved in ether, the ethereal solution washed with dilute sodium hydroxide, and dried. After the removal of the solvent, the oil solidified, and was crystallised from methyl alcohol, in which the substance is moderately readily soluble. The slender, colourless needles melted at  $109^{\circ}$ :

0.1675 gave 0.4722  $\text{CO}_2$  and 0.0859  $\text{H}_2\text{O}$ .  $\text{C}=76.9$ ;  $\text{H}=5.7$ .

$\text{C}_{18}\text{H}_{16}\text{O}_3$  requires  $\text{C}=77.1$ ;  $\text{H}=5.7$  per cent.

The solution in sulphuric acid is colourless and exhibits a faint blue fluorescence, which becomes intense on keeping or on gently heating, and this behaviour appears to be due to sulphonation. There was no evidence in numerous trials that the substance could be converted into a pyrrylium salt containing the indene nucleus.

*Hydrolysis of the Methyl Ether.*—A mixture of the methyl ether (1.5 grams), potassium hydroxide (2 grams), and methyl alcohol (10 c.c.) was heated in a wide test-tube in such a manner as gradually to remove a part of the methyl alcohol by distillation. A characteristic crimson coloration soon appeared and reached a maximum, after which it very quickly faded. When the solution or fusion had just lost the last trace of the red colour and had become yellow, the reaction was considered to be complete, and the mixture, together with the methyl-alcoholic distillate, was submitted to distillation in a current of steam. The aqueous distillate had the odour of benzylacetone, and the semicarbazone of the latter was prepared from it. This substance crystallised from alcohol in slender, colourless needles melting at  $145^{\circ}$  (Klages, *Ber.*, 1904, **37**, 2313, gives  $142^{\circ}$ ), and at the same temperature when mixed with a purified specimen of the semicarbazone obtained from benzylacetone prepared by the reduction of phenyl styryl ketone by hydrogen in the presence of palladium. The alkaline solution remaining in the flask was rendered acid by the addition of hydrochloric acid, and then alkaline again with sodium carbonate. The oil precipitated by the acid did not redissolve, but soon solidified and was collected and crystallised from methyl alcohol, when it was obtained in colourless needles melting at  $105^{\circ}$ , and at the same temperature when mixed with a specimen of 2-hydroxy-4-methoxy-phenyl phenylethyl ketone. The aqueous solution from which this substance had been separated was extracted with ether in order to remove further traces of the same compound; it was then concentrated and acidified, when a small amount of slender needles separated. The substance gave an intense violet colour with ferric chloride in aqueous solution, and melted at  $155^{\circ}$ . The melting point was not depressed when the substance was mixed with 2-hydroxy-4-methoxybenzoic acid obtained by the methylation of  $\beta$ -resorcylic acid.

#### *Methylation of Resacetophenone.*

The following is a brief account of our observations in this connexion. The methylation to paeanol is advantageously effected by means of methyl iodide and potassium hydroxide in boiling methyl-alcoholic solution, and 10 per cent. more than the theoretically

required amount of each reagent suffices. If for each molecular proportion of resacetophenone three molecular proportions of methyl iodide and potassium hydroxide are employed, the main product is the dimethyl derivative, melting at 83–84° (Gregor, *Monatsh.*, 1894, 15, 437; Wechsler, *ibid.*, 15, 239; A. G. Perkin, T., 1895, 67, 996), which has one of the methyl groups in the aromatic nucleus. An attempt was made to divide the operation of methylation into two parts, that is, to methylate first to paeanol and then to attempt the further conversion of this ether into the substance melting at 83–84°. When, however, paeanol was treated with two molecular proportions of methyl iodide and potassium hydroxide in boiling methyl alcohol, the greater part of the substance was recovered unchanged, and the small yield of product insoluble in cold sodium hydroxide solution was a mixture of about equal proportions of dimethylresacetophenone (m. p. 83–84°) and the normal dimethyl ether. The two substances could be separated by means of warm dilute sodium hydroxide, in which the former dissolves. This rather unexpected result renders it clear that the methylation of resacetophenone precedes the *O*-methylation in the case where an excess of methyl iodide and potassium hydroxide is employed. Probably the explanation is that, in the case of the dipotassium salt, methylation occurs at the carbon atom, whereas in the case of the monopotassium salt the *O*-ether is formed. If methyl sulphate is employed for the methylation, it is difficult to obtain a satisfactory yield of paeanol, and the substance melting at 83–84° is not obtained, but, instead, the normal dimethyl ether of resacetophenone.

A simple qualitative test which may be used to indicate the presence or absence of the nuclear methyl group in resorcinol derivatives of the type of resorcylic acid or resorcinol ketones depends on the formation of homofluorescein or fluorescein respectively. The substance is strongly heated with an excess of phthalic anhydride and a few drops of sulphuric acid, and the product dissolved in dilute sodium hydroxide. Fluorescein is formed under these conditions from most resorcinol derivatives, even if they are alkylated at the oxygen atom and the appearance of the alkaline solution is well known. If the resorcinol nucleus contains the methyl group, however, the alkaline solution is intense cherry-red, and the fluorescence is less persistent on dilution than is the case with fluorescein itself.

*2-Hydroxy-4-methoxyphenyl Phenylethyl Ketone (IX).*

We have carefully repeated the work of Bargellini and Marantoni (*loc. cit.*) on the methylation of 2:4-dihydroxyphenyl phenylethyl ketone, and have failed to obtain the so-called monomethyl ether melting at 74–75°. On the other hand, the prescription given for the preparation of the dimethyl ether works well, and the product is the real monomethyl ether. The substance crystallised from alcohol in colourless needles melting at 105°:

0.1635 gave 0.4491 CO<sub>2</sub> and 0.0927 H<sub>2</sub>O. C=74.9; H=6.3.

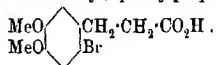
0.4126 „ 0.3690 AgI. MeO=11.9.

C<sub>16</sub>H<sub>16</sub>O<sub>3</sub> requires C=75.0; H=6.3; MeO=12.1 per cent.

The same substance was obtained by the methylation of 2:4-dihydroxyphenyl phenylethyl ketone by means of half the theoretical amount of methyl sulphate, and also by employing methyl iodide. It was insoluble in aqueous sodium carbonate or sodium hydroxide in the cold, but dissolved in the latter on heating. It gives an intense reddish-violet coloration on the addition of ferric chloride to its alcoholic solution. Attempts to convert the substance into definite acetyl or benzoyl derivatives were unsuccessful, and we were unable to obtain its methyl ether. The constitution of the compound is best demonstrated by the following method of preparation.

Benzylidenepaeanol (Emilewicz and Kostanecki, *Ber.*, 1899, 32, 312) could be reduced by hydrogen in the presence of palladium in ethereal or alcoholic solution, but the latter was more convenient in practice. The chalkone (5 grams) was dissolved in ethyl alcohol (250 c.c.) at from 50–60°, and the air in the flask containing the solution was then expelled by purified hydrogen, after which palladous chloride solution (15 c.c. of 1 per cent.) and gum arabic (15 c.c. of 1 per cent. solution) were added. The flask was then closed, vigorously shaken by mechanical means, and connected to the hydrogen generator.

The reduction proceeded rapidly and could easily be followed by noting the rapidity of the stream of hydrogen which passed through the wash-bottles. After twenty minutes, the gas was no longer absorbed, and this was coincident with the disappearance of the yellow colour of the alcoholic solution. The greater part of the alcohol was removed from the filtered solution by distillation, and on cooling, the concentrate deposited 4.8 grams of needles melting at 105°. The substance melted at the same temperature when intimately mixed with a specimen obtained by the methylation of 2:4-dihydroxyphenyl phenylethyl ketone.

6-Bromo-3:4-dimethoxy-*B*-phenylpropionic Acid,

The condensation of 3:4-dimethoxyphenylpropionic acid and resoreinol in the presence of zinc chloride did not give useful results, probably owing to the ease with which the acid undergoes internal dehydration with the formation of dimethoxyhydrindone. It was thought that the bromo-acid would be more amenable to this reaction, but such did not prove to be the case.

3:4-Dimethoxyphenylpropionic acid was brominated in cold acetic acid solution by means of a molecular proportion of bromine dissolved in the same solvent. A part of the product crystallised and the remainder was obtained on the addition of water. The substance was crystallised from aqueous acetic acid and obtained in clusters of needles melting at 123°:

0.0916 required for neutralisation 0.01778 KOH.

This amount of a monobasic acid,  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{Br}$ , requires 0.01772 KOH.

This acid is converted by phosphoric oxide in boiling benzene solution into a hydrindone derivative, which yields a very sparingly soluble piperonylidene derivative.

2-Hydroxy-4-methoxyphenyl 3:4-Dimethoxyphenylethyl Ketone  
(*Dihydrobutein Trimethyl Ether*), VII.

Veratrylidene-paeanol (A. G. Perkin and Hummel, *loc. cit.*) was found to be more difficult to reduce than the benzylidene derivative, and ether, alcohol, and ethyl acetate were all found to be unsuitable solvents. Ultimately, acetic acid was successfully employed, and the addition of a protective colloid, such as gum arabic, was omitted. The chalcone (5 grams), dissolved in acetic acid (450 c.c.), heated to 70–80°, was reduced by shaking with hydrogen after the addition of palladous chloride solution (20 c.c. of 1 per cent.). The absorption of gas slackened after half an hour, but, as the reaction did not appear to be complete, the liquid was again heated to 70–80° and 10 c.c. of the palladous chloride solution were added. The reduction was then completed by shaking with hydrogen for an hour. The colourless solution was filtered from the palladium-black and the acetic acid recovered by distillation under diminished pressure. Brine was added to the residue, and the colourless solid which was precipitated was collected, washed with water, and crystallised from methyl alcohol.

The substance crystallised in stout, colourless prisms melting at  $84^{\circ}$ , and the yield was 80 per cent. of that demanded by theory:

0.1400 gave 0.3512  $\text{CO}_2$  and 0.0879  $\text{H}_2\text{O}$ .  $\text{C}=68.4$ ;  $\text{H}=6.5$ .

$\text{C}_{15}\text{H}_{20}\text{O}_3$  requires  $\text{C}=68.4$ ;  $\text{H}=6.3$  per cent.

The coloration in alcoholic solution produced by the addition of a drop of ferric chloride is almost identical with that obtained in the case of ethyl acetoacetate. The substance is converted by dilute aqueous sodium hydroxide into a very sparingly soluble, voluminous sodium salt, but this is decomposed in the presence of ether, which extracts the free enol.

#### *Synthesis of isobrazilein Ferrichloride Trimethyl Ether.*

A mixture of the compound just described (3 grams), fused zinc chloride (5 grams), and anhydrous formic acid (20 grams) was boiled for three hours under reflux. After a short time, the solution assumed a red colour and green fluorescence, and this became much intensified as the reaction proceeded. After cooling, dilute hydrochloric acid and an excess of concentrated ferric chloride solution were added, and a dark brown, viscid mass was precipitated. This was collected, freed as far as possible from adhering liquid, and then dissolved in hot acetic acid. As the solution cooled, pale brown, glistening needles with metallic gloss separated, which were collected and purified by recrystallisation from acetic acid. Half a gram of the pure substance was obtained. In some respects, this synthesised material did not appear to be identical with isobrazilein ferrichloride trimethyl ether, which, as usually obtained (Engels, Perkin, and Robinson, *loc. cit.*, p. 1131) crystallises in magnificent copper leaflets, and it seemed at first sight necessary to conclude that the two substances were different. The reactions of the two specimens were, however, very similar except with dilute aqueous sodium hydroxide, which in the case of the copper leaflets developed a reddish-purple colour. From previous experience, we surmised that this reaction must be due to the presence of phenolic groups, since the pyranol bases from methyl oxyanhydropyranol salts are colourless and insoluble in alkaline solutions. Since, in addition, microscopic examination of the copper leaflets showed that the crystals had curved edges, it became very probable that the substance obtained from brazilein was contaminated with a small proportion of a demethylated salt, the result of the action of the concentrated sulphuric acid used in the operation. This view was proved to be correct, since by exercising great care in the preparation we obtained the salt from brazilein in the same crystalline form as characterised the synthesised spe-

men. The tetramethyldihydrobrazileinol employed in the preparation was repeatedly purified by solution in light petroleum, as described by Engels, Perkin, and Robinson (*loc. cit.*), and ground in a mortar with excess of cold sulphuric acid for only ten minutes. The sulphate and hydrochloride were then isolated as already described, and the anhydroferrichloride was prepared from the latter in hot aqueous-alcoholic hydrochloric acid solution. The precipitated salt was recrystallised from acetic acid, and in this way a specimen was obtained which was identical in all respects with the material synthesised in the manner described above. The whole of the following observations were made with both specimens, and the two experiments carried out side by side and as nearly as possible under the same conditions. In all cases, complete identity of behaviour was recorded; all the colours appeared at the same stage; turbidity, fluorescence, and behaviour on dilution were always the same. The crystals are well-defined, pointed needles, transparent under the microscope, and in mass are pale ochreous-brown and have a coppery lustre. A suspension of the crystals in acetic acid has a characteristic appearance. If crystallised rapidly by cooling a concentrated solution in hot acetic acid, the tendency is for two or three needles to form a cluster, and at the ends of each of the larger needles a great number of very small needles collect. The substance has no definite melting point, it darkens at 180°, and above this temperature decomposition is progressive; from 203° to 215° there was shrinking and melting accompanied by decomposition. On breaking the capillary tubes, the contents were greenish-black and had a green lustre. The solubility of the substance in various solvents was noted. It does not dissolve in alcohol in the cold to any appreciable extent; on warming, the alcohol acquires an apple-green fluorescence, and, on boiling, the fluorescence is intense ivy-green and the solution becomes yellowish-brown. An aqueous solution of the substance is at first yellow and exhibits brilliant green fluorescence. On keeping, the salt is hydrolysed and the solution becomes slightly milky, the original appearance being restored by the addition of a few drops of hydrochloric acid. 0.1 Gram dissolves to a clear solution in 100 c.c. of water with the addition of 0.5 c.c. of concentrated hydrochloric acid. The behaviour of this solution on dilution was noted, and the fluorescence was found to be remarkably persistent. The addition of sodium acetate to the aqueous solution destroyed the fluorescence, and the pyranol base could be extracted by ether. The ethereal layer was very pale yellow, and the yellow, strongly fluorescent hydrochloride was regenerated by washing it with dilute hydrochloric acid. On the addition of nitric acid to the solution



of the substance in water, the first appearance was the loss of fluorescence and the production of a bright cherry-red colour. On keeping, the colour became yellow, and the fluorescence reappeared and was even more intense than that of the original solution. On the addition of sodium hydroxide to a solution of the ferrichloride, a faint cherry-red opalescence resulted; on shaking with air, a brownish-red solution and precipitate were obtained.

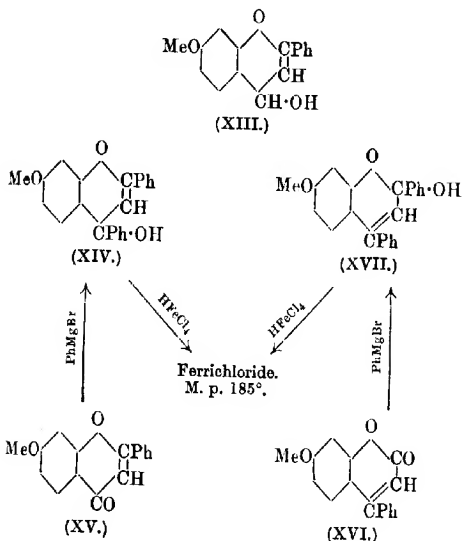
#### APPENDIX I.

##### *Some Anhydropyranol Salts.*

By ROBERT ROBINSON and MAURICE RUSSELL TURNER.

ABOUT ten years ago the authors carried out a series of experiments in the benzopyranol group with the object of determining the nature of the pyranol bases and of discovering the cause of the intense colour which characterises some of these substances. It was found that the coloured pyranol bases are all quinones, occasionally retaining tenaciously a molecule of water, and thus appearing to be carbinols. Several of these quinones were isolated in a pure condition, and it is hoped at some future time to publish an account of the investigation. In order to prove that the true carbinols are colourless, we prepared methyl ethers, and it is in connexion with these substances that certain points were noted which are of interest in relation to the foregoing communication. It is especially interesting that anhydro-salts of 7-methoxy-2-phenyl-1:4-benzopyranol (XIII) and of 7-methoxy-2:4-diphenyl-1:4-benzopyranol (XIV) dissolve in water with an intense bluish-green fluorescence, and in this respect closely resemble the similarly constituted *isobrazilein* hydrochloride trimethyl ether, but, on the other hand, differ from related hydroxy-compounds. The former substance (XIII) was obtained by the application of the general method for the preparation of anhydropyranol salts devised by Perkin, Robinson, and Turner (T., 1908, **93**, 1115), namely, by the condensation of 2-hydroxy-4-methoxybenzaldehyde with acetophenone in acetic acid solution by means of hydrogen chloride. The second compound (XIV) was obtained by the condensation of dibenzoylmethane with the monomethyl ether of resorcinol in the presence of sulphuric acid, but it was found impossible to obtain it by this method free from the corresponding demethylated compound, and the benzopyranol prepared from the salt was always red. This method of preparation has already been described by Becker and Decker (*Ber.*, 1914, **47**, 2288).

In order to obtain the substance in a pure condition, three methods could be employed, and are described on p. 877. As was to be expected, the compound (XIV) may be prepared by the action of magnesium phenyl bromide on 7-methoxy-2-phenyl-1:4-benzopyrone (XV), and was isolated from the product in the form of the anhydroferrichloride melting at 185°. The same anhydroferrichloride was, however, obtained from the product of interaction of magnesium phenyl bromide and  $\beta$ -phenylumbelliferone methyl ether (XVI). This would seem to demonstrate the possibility of the existence of two carbinol bases corresponding with a single anhydro-oxonium salt, since the process last mentioned should lead to the  $\alpha$ -pyranol (XVII).



#### EXPERIMENTAL.

##### 7-Methoxy-4-phenyl-1:2-benzopyrone ( $\beta$ -Phenylumbelliferone Methyl Ether), XVI.

1. A mixture of resorcinol monomethyl ether (13 grams) and ethyl benzoylacetate (20 grams) was dissolved in ice-cold sulphuric acid (200 grams). The flask was immersed in melting ice and allowed to remain for twelve hours. The viscid product obtained by dilution with water was well washed, and became solid in con-

tact with a little alcohol. The substance was collected and re-crystallised from alcohol.

*B.  $\beta$ -Phenylumbelliferone* was methylated in the usual manner in methyl-alcoholic solution by means of methyl sulphate and potassium hydroxide. At the end of the reaction, however, an excess of hydrochloric acid was added and the solution boiled in order to convert into lactone any hydroxy-acid which had been formed as the result of the hydrolysing action of the alkali. After the addition of water, the substance was collected and crystallised from alcohol; it is moderately readily soluble in alcohol or benzene, and crystallises in slender needles which melt at  $110^{\circ}$ . The pale yellow solution in sulphuric acid exhibits intense bluish-violet fluorescence:

0.1255 gave 0.3489  $\text{CO}_2$  and 0.0560  $\text{H}_2\text{O}$ .  $\text{C}=75.8$ ;  $\text{H}=4.9$ .

$\text{C}_{16}\text{H}_{12}\text{O}_3$  requires  $\text{C}=76.2$ ;  $\text{H}=4.7$  per cent.

*2:4-Dimethoxydibenzoylmethane and 7-Methoxy-2-phenyl-1:4-benzopyrone (XV).*

2:4-Dimethoxydibenzoylmethane has already been obtained by Perkin and Schiess (T., 1904, 85, 164) by the condensation of methyl 2:4-dimethoxybenzoate with acetophenone in the presence of metallic sodium. Since, however, we happened to be in the possession of large quantities of 2:4-dimethoxyacetophenone, we employed this compound as the starting point. 2:4-Dimethoxyacetophenone (55 grams) and ethyl benzoate (90 grams) were dissolved in dry ether (250 c.c.), and powdered sodamide (50 grams) was gradually added to the solution. A vigorous reaction ensued and the colourless sodium salt of the diketone separated as a crust. After gently boiling under reflux for half an hour, the salt was separated and washed with ether, and, when dry, was triturated in a mortar with dilute hydrochloric acid. The oily product soon became solid and crystalline in contact with fresh cold water, and was collected, washed with sodium carbonate solution, dried, and crystallised from light petroleum. The pale yellow needles melted at  $57^{\circ}$ :

0.1403 gave 0.3683  $\text{CO}_2$  and 0.0758  $\text{H}_2\text{O}$ .  $\text{C}=71.6$ ;  $\text{H}=6.0$ .

$\text{C}_{17}\text{H}_{16}\text{O}_4$  requires  $\text{C}=71.8$ ;  $\text{H}=5.6$  per cent.

When this diketone is mixed with ten times its weight of hot hydriodic acid (D 1.9), an immediate reaction occurs, methyl iodide is evolved, and the flavone derivative separates. The process is remarkably smooth. After removing the free iodine by the addition of sulphurous acid, the precipitate was collected and crystallised from alcohol. It melts at  $110^{\circ}$ , and is doubtless identical

with the compound obtained by Emilewicz and Kostanecki (*loc. cit.*) by the action of alkali on benzyldenepaeanol dibromide. The intensity of the blue fluorescence of the solution of this flavone in sulphuric acid is noteworthy.

*7-Methoxy-2-phenyl-1:4-benzopyranol Anhydrohydrochloride.*  
(*Anhydrohydrochloride of XIII.*)

2-Hydroxy-4-methoxybenzaldehyde (8 grams) and acetophenone (6 grams) were dissolved in glacial acetic acid (25 c.c.), and the solution was saturated with hydrogen chloride during an hour and a-half. The orange needles which separated were collected, and more of the substance was obtained by the addition of ether to the solution. The salt could be recrystallised from dilute hydrochloric acid, and, after being dried in the air, melted and decomposed at 102–103°:

0.1155 gave 0.2506  $\text{CO}_2$  and 0.0606  $\text{H}_2\text{O}$ .  $\text{C}=59.2$ ;  $\text{H}=5.8$ .

$\text{C}_{16}\text{H}_{13}\text{O}_2\text{Cl}, 3\text{H}_2\text{O}$  requires  $\text{C}=58.8$ ;  $\text{H}=5.8$  per cent.

The substance dissolves in water to a yellow solution exhibiting a striking bluish-green fluorescence, extremely persistent on dilution.

*7-Methoxy-2:4-diphenyl-1:4-benzopyranol and its Salts.*

A. 7-Hydroxy-2:4-diphenyl-1:4-benzopyranol dimethyl ether (Bülow and Sicherer, *Ber.*, 1901, **34**, 2380) loses methyl alcohol on treatment with acids, and yields salts of the monomethylated pyranol. The ferrichloride was obtained in the usual manner, and crystallised from acetic acid in orange-yellow needles melting at 185°, and at the same temperature when mixed with the salt obtained as described under *B* and *C*. The fluorescence of the dimethyl ether in acetic or sulphuric acid solution is due to the conversion to an oxonium salt of the pyranol now under consideration.

B.  $\beta$ -Phenylumbelliferone methyl ether (2 grams) was dissolved in hot benzene (50 c.c.) and treated with a solution of magnesium phenyl bromide in ether until a test portion developed an intense bluish-green colour on the addition of an ethereal solution of *p*-benzoquinone. The mixture was then heated on the steam-bath for ten minutes, cooled, and decomposed with water. The benzene solution contained a substance which is probably an  $\alpha$ -pyranol, and gave an oxonium salt on the addition of hydrochloric acid. In order to isolate this, the whole product was treated with dilute hydrochloric acid, and the separated yellow, aqueous layer mixed

with an excess of concentrated ferric chloride solution. The precipitated yellow ferrichloride was crystallised from acetic acid and obtained in orange needles melting at  $185^{\circ}$ .

*C.* 7-Methoxyflavone (4 grams) dissolved in benzene (150 c.c.) was mixed with an ethereal solution of magnesium phenyl bromide (from 1.8 grams of bromobenzene). A yellow precipitate was formed, and after gently heating on the steam-bath for fifteen minutes, the mixture was decomposed by dilute hydrochloric acid. A copious precipitate of the ferrichloride was obtained on the addition of ferric chloride to the aqueous layer, and the derivative was collected and crystallised from acetic acid. The orange-yellow needles melted at  $185^{\circ}$ :

0.1469 gave 0.2783  $\text{CO}_2$  and 0.0475  $\text{H}_2\text{O}$ .  $\text{C}=51.7$ ;  $\text{H}=3.6$ .  
0.3600 „ 0.0572  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=11.1$ .

$\text{C}_{22}\text{H}_{17}\text{O}_3\text{Cl}_2\text{FeCl}_3$  requires  $\text{C}=51.7$ ;  $\text{H}=3.3$ ;  $\text{Fe}=11.0$  per cent.

The pyranol itself and its derivatives could most conveniently be obtained by the method *A*.

7-Methoxy-2 : 4-diphenyl-1 : 4-benzopyranol.—Bülow and Sicherer's dimethyl ether was dissolved in dilute hydrochloric acid and the solution treated with sodium acetate. The almost colourless precipitate was amorphous, but was obtained in a pure condition by washing with water and drying in a vacuum over sulphuric acid. It melted at  $55-57^{\circ}$ :

0.1323 gave 0.3862  $\text{CO}_2$  and 0.0702  $\text{H}_2\text{O}$ .  $\text{C}=79.6$ ;  $\text{H}=5.9$ .  
0.1962 in 19.9 benzene gave  $\Delta^d=0.153^{\circ}$ .  $\text{M.W.}=322$ .  
 $\text{C}_{22}\text{H}_{18}\text{O}_3$  requires  $\text{C}=80.0$ ;  $\text{H}=5.5$  per cent.  $\text{M.W.}=330$ .

*Anhydrodihydrochloride*.—Dry hydrogen chloride was passed through an ethereal solution of the pyranol. Bright yellow crystals melting at  $121^{\circ}$  separated, and were dried in a vacuum:

0.2264 gave 0.1576  $\text{AgCl}$ .  $\text{Cl}=17.2$ .  
 $\text{C}_{22}\text{H}_{15}\text{O}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  requires  $\text{Cl}=16.9$  per cent.

Direct proof of the existence of the water of crystallisation was not obtained.

*Anhydrodihydrochloride*.—The dihydrochloride was dissolved in hot dilute hydrochloric acid, and the solution, on cooling, deposited red needles melting indistinctly at about  $80^{\circ}$ :

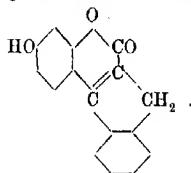
0.2148 gave 0.0900  $\text{AgCl}$ .  $\text{Cl}=10.4$ .  
 $\text{C}_{22}\text{H}_{17}\text{O}_2\text{Cl}$  requires  $\text{Cl}=10.2$  per cent.

*Anhydrotatinichloride*.—This derivative was prepared in a hot solution, and crystallised, on cooling, in orange needles melting and decomposing at  $224^{\circ}$ :

0.2419 gave 0.0455 Pt. Pt=18.8.

$(C_{20}H_{17}O_2Cl)_2PtCl_4$  requires Pt=18.9 per cent.

## APPENDIX II.

*7-Hydroxy-4:3-indeno-1:2-benzopyrone,*

This substance was prepared in 1911 by Mr. J. A. Prescott working in collaboration with one of us in the laboratories of the University of Manchester. Although the work was not carried far, it seems of interest to include a description of this substance in the present communication in view of the circumstance that it is the first compound to be synthesised the molecule of which contains the brazilin and hæmatoxylin skeleton.

$\alpha$ -Hydrindone (8.5 grams) dissolved in pure dry ether (100 c.c.) was converted into the sodium derivative by the addition of powdered sodamide (6 grams). The evolution of ammonia was facilitated by frequent shaking, and the reaction appeared to be complete in about two hours. A rather rapid stream of carbon dioxide was then passed through the solution until the ether had nearly all been removed by evaporation. Ice was then carefully added and the solution extracted twice with ether to remove a small amount of unchanged hydrindone. The separated aqueous layer was then acidified with hydrochloric acid with careful cooling by small pieces of ice. The crystalline precipitate was quickly collected and dried on porous porcelain. The yield of this *hydrindone-2-carboxylic acid* was 8 grams. The substance gives a reddish-violet coloration on the addition of ferric chloride to its aqueous or alcoholic solution. It is moderately stable at the ordinary temperature, but slowly decomposes with the formation of  $\alpha$ -hydrindone and carbon dioxide. The reaction is rapid and complete on gently warming with water. The keto-acid (8.3 grams), together with resorcinol (9 grams), was mixed with a saturated solution (100 c.c.) of hydrogen chloride in methyl alcohol. The mixture was allowed to remain during two and a-half days at the ordinary temperature, when it became red, and a colourless substance crystallised. The liquid was then gently heated for two hours on the water-bath, and the quantity of the crystals was

increased. When cold, the substance was collected and crystallised from ethyl alcohol, from which it separated in colourless needles, the yield amounting to 2.1 grams:

Found: C=76.4; H=4.2.

$C_{16}H_{10}O_8$  requires C=76.8; H=4.0 per cent.

On heating, the substance darkens at about  $230^{\circ}$ , and at  $280^{\circ}$  rather suddenly turns dark blue, but does not melt at this or higher temperatures. It is sparingly soluble in most organic solvents, but dissolves in dilute sodium hydroxide. The solution in concentrated sulphuric acid exhibits an intense bluish-violet fluorescence.

UNIVERSITY OF LIVERPOOL.

[Received, September 23rd, 1918.]

### LXXIX.—*The Action of Chlorine on the Alkali Iodides.*

By WILLIAM NORMAN RAE.

In a previous communication (T., 1915, **107**, 1286), an account was given of the action of bromine vapour on the solid iodides of the alkali metals, and the action of chlorine on the same compounds has now been studied.

The alkali metals form two series of polyhaloids containing both chlorine and iodine, having, respectively, the formulæ  $MICl_2$  and  $MICl_4$ ; all the compounds of the latter series were prepared in the wet way by Wells and Wheeler (*Amer. J. Sci.*, 1892, [iii], **44**, 42), who found that two of them gave hydrated crystals, namely,  $LiICl_4 \cdot 4H_2O$  and  $NaICl_4 \cdot 2H_2O$ , whilst the others were anhydrous. The compounds  $KICl_4$  and  $NH_4ICl_4$  were originally prepared by Filhol (*J. Pharm.*, 1839, **25**, 435, 506).

In the present instance, the method of experiment was as follows: the iodides were powdered and kept in a desiccator over sulphuric acid for several weeks before using, to ensure thorough dryness; a small quantity was then placed in a weighing bottle having a ground-in glass stopper, through which passed two tubes one of which reached nearly to the bottom of the bottle. During the weighings, the two tubes were closed with ground-in glass stoppers. Several of the bottles were connected in series, and a slow stream of chlorine, washed in water and dried with sulphuric acid, was passed through the train of bottles, and finally through

a calcium chloride tower, used to prevent moisture diffusing back in case the chlorine stream stopped. The bottles were weighed from day to day until the weight became constant, and the contents were then analysed. In all cases, the compound  $MICl_4$  appeared to be formed. The compound  $MICl_2$  for a given metal is much more stable than  $MICl_4$ , as is indicated by the well-marked breaks in the curves showing the loss of weight over potassium hydroxide with time, given in the previous paper (*loc. cit.*), and it might be expected that similar breaks would be obtained in the "increase of weight-time" curves in the present instance, the formation of the more stable compound  $MICl_2$  proceeding more rapidly than that of the compound  $MICl_4$ . Such breaks, however, were not obtained, although there was a considerable diminution in the speed of the reaction towards the end, when the formation of the final compound was almost complete. Apparently the formation of the two compounds proceeds simultaneously, or the compound  $MICl_4$  is formed without the intermediate formation of  $MICl_2$ ; in this connexion, it may be remembered that Wells and Wheeler (*loc. cit.*) considered that the compound  $RhCl_4$  decomposes at the ordinary temperature by the loss of iodine trichloride in one step, whilst at higher temperatures it loses first chlorine and then iodine monochloride; this is supported by the fact that when potassium tetrachloroiodide and mercury are placed in the same desiccator, mercuric iodide is formed. Again, it was expected that the stability of the various compounds would be indicated by the rate at which they were formed, but the reverse was the case; for example, in one experiment the first three tubes contained the iodides of caesium, rubidium, and potassium, respectively; this is also the order of stability of the chloroiodides; after two days it was found that 1.27 grams of caesium iodide had gained 0.10 gram, 0.65 gram of rubidium iodide had gained 0.40 gram, 1.67 grams of potassium iodide had gained 0.23 gram.

Several factors appear to affect the rate of formation besides the stability of the product; one of the most important is the degree of dryness of the solid iodide; an immediate increase in the rate of change follows the introduction of a trace of water, whilst lithium iodide, containing three molecules of water of crystallisation, always reacts rapidly. Rapid reactions are also obtained by using finely powdered solid in thin layers; with thick layers or crystals, the reaction takes place quickly at the surface, but only slowly throughout the mass.

The best quantitative results are obtained by using a slow stream of chlorine and a small quantity of solid; with larger quantities,



the initial displacement of the iodine in the iodide by chlorine proceeds rapidly, with the evolution of much heat (greatest in the case of lithium iodide and least with caesium iodide), so that the liberated iodine is partly vaporised and is lost; at a slower rate, the temperature does not appreciably rise; with iodides such as those of rubidium and caesium, the iodine at first set free appears to combine with the unchanged iodide to form the tri-iodides, which have a low vapour pressure. All the compounds obtained by this method are yellow powders; the colour shows a marked gradation with the atomic weight of the metal, the caesium compound being a mustard-yellow, whilst that formed from lithium iodide is a fine deep orange.

*Lithium Iodide.*—The anhydrous compound has not been obtained in a pure state; the compound  $\text{LiI} \cdot 3\text{H}_2\text{O}$  was therefore prepared, and the crystals, dried on filter-paper, were used, since the substance is too deliquescent to powder. At the same time, another part of the specimen was analysed. (Found:  $\text{I} = 68.7$ . Calc.,  $\text{I} = 67.5$  per cent.)

0.8526 Gram of the crystals gained 0.6549 gram of chlorine, a gain of 76.8 per cent., whilst the theoretical gain is 76.7 per cent. for the formation of  $\text{LiICl}_4 \cdot x\text{H}_2\text{O}$  from  $\text{LiI} \cdot x\text{H}_2\text{O}$ , containing 68.7 per cent. of iodine. On analysis by titration with arsenite solution, the amount of chlorine gained by the lithium iodide was found to be 71.8 per cent., and with a second preparation, 71.7 per cent.

When the chlorine first comes in contact with the lithium iodide, the latter becomes deep reddish-brown and moist on the surface; the crystals then melt and much heat is evolved, but there are no copious fumes of iodine chloride as there are in the case of iodine itself; liquid drops do appear on the sides, but these are only faintly coloured and are probably drops of moisture vaporised by the heat of the reaction. Finally, the whole is converted into an orange-coloured solid. The melting is due to the fact that the lithium iodide contains enough water to dissolve the lithium chloride which is formed at first, whilst both lithium iodide and the chloriodide melt below  $80^\circ$ . The final compound is a solid at the ordinary temperature. Wells and Wheeler have shown that the crystals obtained from solution have the formula  $\text{LiICl}_4 \cdot 4\text{H}_2\text{O}$ , whilst in the present case there is only enough water to give the compound  $\text{LiICl}_4 \cdot 3\text{H}_2\text{O}$ . The reaction was complete in two days.

*Ammonium Iodide.*—The salt was recrystallised from water, and was then heated in an air-oven at  $150^\circ$  for some time, and was kept in the desiccator until required. Chlorine quickly changed it to bluish-black by displacing the iodine, and then the yellow

colour of the iodochloride appeared. The weight became constant in two or three days. 1.1512 Grams of ammonium iodide gained 1.1151 grams of chlorine, corresponding with 96.86 per cent., whilst the formation of  $\text{NH}_4\text{ICl}_4$  requires a gain of 97.85 per cent. A determination of the extra halogen by the arsenite method gave a result corresponding with a gain of 95.94 per cent., a second preparation giving 94.99 per cent.

*Sodium Iodide.*—The salt was recrystallised from water in a desiccator over sulphuric acid. The crystals so obtained were powdered and replaced in the desiccator until used. The reaction followed a similar course to that with ammonium iodide, but a longer time was required to reach constant weight. In two experiments, 0.7587 gram gained 0.6927 gram, or 91.3 per cent., and 0.7956 gram gained 0.7439 gram, corresponding with 93.50 per cent.;  $\text{NaICl}_4$  requires a gain of 94.61 per cent. A specimen analysed by sodium arsenite gave 92.77 per cent.

*Potassium Iodide.*—The salt was recrystallised from water, dried, and powdered. Results similar to those with the previous two compounds were obtained, but in some cases a long time was required to reach constancy of weight. 1.0727 Grams of potassium iodide gained 0.9111 gram, equivalent to 84.94 per cent.; analysis by sodium arsenite gave extra halogen equivalent to a gain of 82.31 per cent., whilst the formation of  $\text{KICl}_4$  requires 85.44 per cent.

*Rubidium Iodide.*—The salt was prepared by repeated evaporation of the chloride with hydriodic acid, and was then recrystallised from water. On coming in contact with chlorine, it first turned bluish-black and then yellow; in one experiment, the formation of the yellow compound did not commence simultaneously over the whole surface, but at a number of points, which appeared to act as nuclei, giving a very striking appearance of a number of bright yellow spots on a bluish-black background. 0.6545 Gram gained 0.4366 gram of chlorine, corresponding with 66.7 per cent., whilst  $\text{RbICl}_4$  requires a gain of 66.8 per cent. Since very little of the rubidium salt was available, it was not analysed by sodium arsenite, but was heated until it was white. 1.0911 Grams of the chloroiodide lost 0.7234 gram of iodine trichloride, a loss of 66.3 per cent. In the conversion of the chloroiodide,  $\text{RbICl}_4$ , to rubidium chloride, the loss should be 65.9 per cent. The formation of the compound proceeded rapidly, and was complete in from three to six days.

*Cæsium Iodide.*—This salt was prepared in the same way as the rubidium compound; the first specimen made reacted very slowly; even the first stages, where the cæsium iodide was being converted

into the chloride, were slow, enabling the change of colour from white, through pale brown, brown, chocolate, to bluish-black to be followed. The pale brown colour observed at the start is possibly due to the formation of polyiodides, the first traces of iodine set free at once uniting with the unchanged caesium iodide, so that the colour of free iodine is not observed until a later stage; the same colour is produced when solid caesium iodide and iodine are shaken together. Compounds such as ammonium tri-iodide are much less stable than caesium tri-iodide, which may account for the fact that the colour of iodine appears as soon as the chlorine comes into contact with ammonium iodide.

A more rapid reaction was obtained in an experiment using a small quantity of finely divided caesium iodide, obtained by preparing the tri-iodide by crystallisation from solution and by heating this at  $180^{\circ}$  until it was quite white. 0.1986 Gram of caesium iodide gained 0.1087 gram of chlorine in six days; the increase in weight corresponds with 54.7 per cent., which is the theoretical gain for the formation of  $\text{CsICl}_4$ . 0.3073 Gram of  $\text{CsICl}_4$  loses 0.1794 gram on heating, corresponding with 58.3 per cent.; the theoretical loss is 58.1 per cent.

CEYLON MEDICAL COLLEGE,  
COLOMBO.

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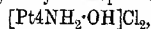
### LXXX.—Hydroxylamine Platinum Bases.

By LEO ALEXANDROWITSCH TSCHUGAEV and ILJA ILJITSCH  
TSCHERNJAEV.

Compounds containing hydroxylamine and platinum were discovered by Lossen (*Annalen*, 1871, **160**, 242), and were studied in more detail by Alexander (*ibid.*, 1893, **246**, 339), and later by Ulenhuth (*ibid.*, 1900, **311**, 120).

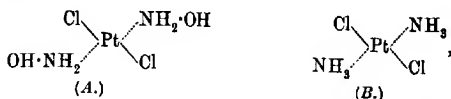
Hydroxylamine, like ammonia, combines with salts of bivalent platinum to form a series of complex compounds which are fairly closely analogous to the well-known ammoniacal platinum bases and to the corresponding derivatives of organic amines, sulphide etc.

Free hydroxylamine and potassium platinochloride interact with the formation of tetrahydroxylaminoplatinous chloride,



an analogue of the salts of Reiset's Base I,  $[\text{Pt}4\text{NH}_3]\text{X}_2$ , and, like

these, this chloride is precipitated by potassium platinochloride to form the compound,  $[\text{Pt}(\text{NH}_2\cdot\text{OH})\text{PtCl}_4]$ , analogous to Magnus's green salt. Further, the chloride is decomposed by heating with hydrochloric acid, with the production of *trans*-dichlorodihydroxylaminoplatinum (A),

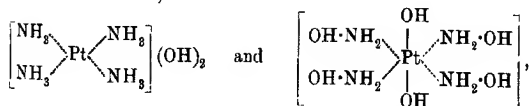


which is similar, in its mode of formation and properties (see appendix), to the chloride of Reiset's Base II (B).

The study of these compounds has shown that hydroxylamine plays the same rôle in the molecule as does ammonia in ammoniacal platinum bases, this conclusion being confirmed by the existence of a mixed base,  $[\text{Pt}2\text{NH}_3\cdot2\text{NH}_2\cdot\text{OH}]\text{X}_2$ , which may be regarded as Reiset's Base I with ammonia partly substituted by hydroxylamine. Some derivatives of this base are described, although very incompletely, by Alexander (*loc. cit.*).

In spite of the very close similarity between the hydroxylamine-platinum bases and the corresponding compounds containing ammonia in place of hydroxylamine, there is a marked difference in their chemical behaviour, as well as in their mode of formation. For example, hydroxylamine is more readily eliminated from the complex platinum compounds than ammonia; it was also not possible to obtain the *cis*-modification of dihydroxylaminoplatinous chloride,  $[\text{Pt}2\text{NH}_2\cdot\text{OH}\cdot\text{Cl}_2]$ , in the usual way, namely, by the interaction of free hydroxylamine and potassium platinochloride, although the corresponding derivatives of ammonia and of organic amines are readily formed by a similar method.

Perhaps the most interesting fact to be noticed in this connexion is that by complete substitution of hydroxylamine for ammonia the very readily soluble compound  $\text{Pt}4\text{NH}_3(\text{OH})_2$ , possessing strong basic properties and analogous to the alkali hydroxides, is transformed into the comparatively weak base  $\text{Pt}4\text{NH}_3\cdot\text{OH}(\text{OH})_2$ , almost insoluble in water and more similar to magnesia. For this reason, it was suggested by Werner ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., 5, 197) that a different constitution,

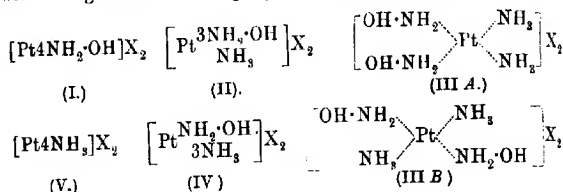


must be attributed to these two bases, the co-ordination numbers

being 4 in the case of Reiset's Base I and 6 in the corresponding hydroxylamine compound.

In view of the great interest attaching to these remarkable facts and relations, we decided to undertake a systematical investigation of the hydroxylamine-platinum bases, and particularly of the mixed bases containing hydroxylamine and ammonia (or amines), in order to elucidate the influence of the progressive substitution of hydroxylamine for ammonia.

Of the six compounds theoretically possible and corresponding with the general formula  $[\text{Pt}(\text{NH}_2\cdot\text{OH})_n(\text{NH}_3)_{4-n}]\text{X}_2$ , only three

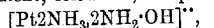


(I, IIIB, and V) have been previously described.

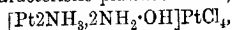
We have succeeded in preparing all the missing members of the series, and have established their constitution and their relation to other hydroxylamino-ammoniacal platinum bases, so far as it was possible in the present state of our knowledge of the chemical constitution of these complex compounds.

Considering first the two isomeric compounds corresponding with the formulae IIIB and IIIB, the chloride of the former, namely, *cis-diamminodihydroxylaminoplatinous chloride* (IIIB, where  $\text{X}=\text{Cl}$ ) may be prepared by the action of free hydroxylamine on *cis*-dichlorodiamminoplatinum (Peyrone's chloride).

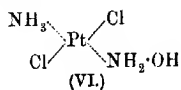
It contains the bivalent, colourless, complex cation



and gives a very characteristic platinochloride,



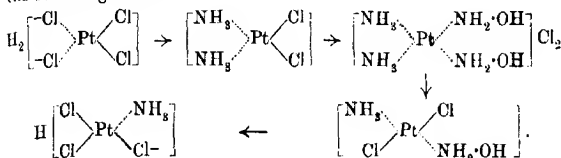
which forms rose-violet, microscopical needles. The constitution of the salts of this series is proved by their mode of formation, by the ionic character of the two electronegative radicles, and by the decomposition of the chloride with hydrochloric acid. In this reaction, the mixed chloride,



is formed in the first stage, and by continued action of the acid the second molecule of hydroxylamine is eliminated, Cossa's acid,

$[\text{Pt}(\text{NH}_3\text{Cl}_2)\text{H}]$ , and finally chloroplatinous acid,  $\text{H}_2[\text{PtCl}_4]$ , being obtained.

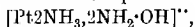
In view of the fact that Peyrone's chloride, the starting point in the preparation of the chloride IIIA, is prepared from chloroplatinous acid and ammonia, it will be seen that the synthesis of the salt IIIA and its degradation form a cycle, as represented by the following scheme:



In the same way, the isomeric salt IIIB may be obtained from the chloride of Reiset's Base II (*B*, p. 885), or by the action of liquid anhydrous ammonia on *trans*-dichlorodihydroxylaminoplatinum (*A*, p. 885).

Possibly the same chloride, in a slightly impure state, was prepared by Alexander by the interaction of *trans*-dichlorodihydroxylaminoplatinum and aqueous ammonia.

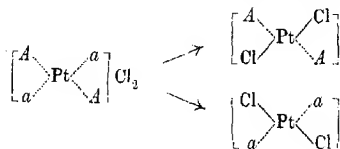
The existence of the divalent complex cation,



in an aqueous solution of the chloride IIIB may be proved by various reactions; for example, potassium platinochloride gives a green platinochloride,  $[\text{Pt}2\text{NH}_3, 2\text{NH}_2\text{OH}]\text{PtCl}_4$ , sparingly soluble in water, and potassium palladochloride and other salts of complex acids act similarly. The chlorine atoms of the chloride IIIB are both ionised in aqueous solution. From these facts, and especially from the mode of formation of this salt, its constitution as *trans*-diamminodihydroxylaminoplatinous chloride (IIIB, where  $\text{X}=\text{Cl}$ ) may be regarded as sufficiently established.

The result of the action of hydrochloric acid on this substance is also in accordance with this conclusion, *trans*-dichlorodiamminoplatinum (*B*, p. 885) being the only product.

According to Jörgensen, the degradation of mixed complex bases corresponding with the *trans*-configuration gives normally two different products, both of which are *trans*-derivatives, thus:



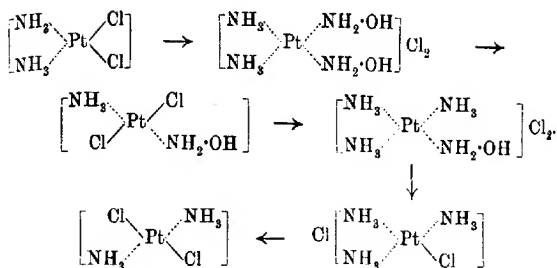
The degradation of the chloride III $\beta$  proceeds, therefore, quite normally in so far as it gives rise to a *trans*-dichloro-derivative with two identical groups A, and the constitution assumed above for this chloride is especially confirmed by the fact that it gives the chloride of Reiset's Base II.

As regards the formation of only one product in this reaction instead of two, it may be remarked that the two compounds obtained by Jörgensen and by others in a series of analogous instances are generally produced in very different relative proportions, according to the degree of stability of the bond uniting the platinum atom with the molecule of ammonia or amine A. In fact, as will be seen later, it appears that a molecule of hydroxylamine is far more loosely combined with the platinum atom than is a molecule of ammonia, and apparently to this difference may be due the discrepancy between Jörgensen's rule and the course of degradation of the chloride III $\beta$ .

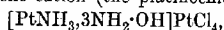
Dichloroamminohydroxylaminoplatinum (VI, p. 886) is a very suitable starting point for the preparation of the two remaining members of our series of mixed ammonia-hydroxylaminoplatinum bases, namely, *amminotrihydroxylaminoplatinous chloride* (II, where X = Cl) and *triaminohydroxylaminoplatinous chloride* (IV, where X = Cl).

The chloride, IV, is best prepared by the interaction of dichloroamminohydroxylaminoplatinum (VI) and liquid ammonia in a sealed tube. Its constitution may be deduced from this mode of formation and from its chemical behaviour. The two chlorine atoms are immediately ionised in aqueous solution, and the complex radicle,  $[\text{Pt}_2\text{NH}_3\cdot\text{NH}_2\cdot\text{OH}]^{++}$ , has the properties of a bivalent cation. By treatment with potassium platinochloride, a green compound,  $[\text{Pt}_3\text{NH}_3\cdot\text{NH}_2\cdot\text{OH}]\text{PtCl}_4$ , analogous to the well-known Magnus's salt, is precipitated.

The most interesting results were obtained by the action of hydrochloric acid on the chloride (IV). The main product of this reaction is Cleve's chloride,  $[\text{Pt}_3\text{NH}_3\text{Cl}]\text{Cl}$ , the molecule of hydroxylamine being displaced by a chlorine atom. This result not only proves the existence of the group  $\text{Pt}_3\text{NH}_3$  in the chloride, IV, but also affords a direct confirmation of the weakness of the bond  $\text{Pt}\dots\text{NH}_2\cdot\text{OH}$  in comparison with the bond  $\text{Pt}\dots\text{NH}_3$ . A more energetic action of hydrochloric acid on Cleve's chloride results, as is well known, in the formation of the chloride of Reiset's Base II. Thus it is possible to effect the conversion of Peyrone's chloride into the isomeric chloride of Reiset's Base II by the following consecutive stages:



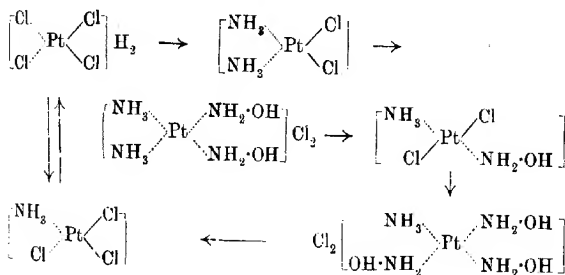
Amminotrihydroxylaminoplatinous chloride (II) is readily obtained from the chloride VI by the action of free hydroxylamine in aqueous solution. The constitution of this chloride follows from its mode of formation, from the inorganic character of the two chlorine atoms, and of the complex radical  $\text{PtNH}_3\cdot 3\text{NH}_2\cdot\text{OH}$ , which forms a bivalent cation (the platinochloride,



was obtained in rose-violet crystals), and especially from the study of its degradation products. By the action of hydrochloric acid, it gives Cossa's acid,  $[\text{PtNH}_3\cdot\text{Cl}_3]\text{H}$ , which then by further action of the acid furnishes chloroplatinous acid.

The relative weakness of the bond  $\text{Pt}\cdots\text{NH}_2\cdot\text{OH}$  is again demonstrated by this reaction.

It will be observed that the formation and degradation of the chloride, II, may also be represented by a cycle:



In addition to the above experiments, the behaviour of the *trans*-chloride,  $[\text{Pt}2\text{NH}_3\cdot\text{OH}\cdot\text{Cl}_2]$ , towards pyridine was studied and found to be in perfect accordance with its behaviour towards ammonia.



The following table gives some physical properties of the mixed chlorides of the series  $[\text{Pt}(\text{NH}_2\text{OH})_n(\text{NH}_3)_{4-n}]\text{Cl}_2$  :—

Compound.	Solubility. (Grams in 100 grams of 71.4 per cent. alcohol.)	Molecular conductivity at 25° V = 1000 litres.	Colour of the corresponding platinichloride.
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ .....	—	261.0	Green (Magnus's salt)
$[\text{Pt}3\text{NH}_3, \text{NH}_2\text{OH}]\text{Cl}_2$ .....	1.36	—	Green
$[\text{Pt}2\text{NH}_3, 2\text{NH}_2\text{OH}]\text{Cl}_2$ ( <i>trans</i> ) .....	0.136	251.0	Dark green
$[\text{Pt}2\text{NH}_3, 2\text{NH}_2\text{OH}]\text{Cl}_2$ ( <i>cis</i> ) .....	0.22	246.0	Reddish-violet
$[\text{Pt}\text{NH}_3, 3\text{NH}_2\text{OH}]\text{Cl}_2$ .....	0.96	200.0	Rose-violet
$[\text{Pt}4\text{NH}_2\text{OH}]\text{Cl}_2$ .....	0.28	—	Lilac

#### EXPERIMENTAL.

*cis*-Diamminodihydroxylaminoplatinous Chloride (IIIa, where X = Cl).

A mixture of 1 gram of Peyrone's chloride, 0.6 gram of hydroxyl ammonium chloride, 3.5 c.c. of 10 per cent. sodium hydroxide solution, and 7 c.c. of water was gently heated with frequent shaking until complete solution occurred. On cooling, the chloride separated in colourless needles or prisms, which were recrystallised from dilute hydrochloric acid and dried in the air:

0.1256 gave 0.0666 Pt. Pt = 53.01.

0.2333 „ 0.1855 AgCl. Cl = 19.67.

0.1832 „ 21.5 c.c.  $\text{N}_2$  (moist) at 20.2° and 776 mm. N = 15.32.

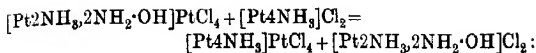
$\text{PtH}_{12}\text{O}_2\text{N}_4\text{Cl}_2$  requires Pt = 53.27; Cl = 19.37; N = 15.30 per cent.

The substance is very readily soluble in water, the chlorine being completely ionised. The molecular conductivity was measured in aqueous solution at 25°:

V .....	125	250	500	1000
$\mu$ .....	226	232	239.5	276

The *platinochloride* separated from a solution of 0.65 gram of the above chloride in 5 c.c. of water on adding a solution of 0.8 gram of potassium platinochloride in 5 c.c. of water. It forms reddish-violet needles, and may be recrystallised from warm water. It is much more readily soluble than the green Magnus's salt.

The insoluble Magnus's salt is precipitated from its aqueous solution on the addition of Reiset's Base I,



0.1119 gave 0.0675 Pt. Pt=60.14.

$\text{Pt}_2\text{H}_{12}\text{O}_2\text{N}_4\text{Cl}_4$  requires Pt=60.22 per cent.

The *palladochloride* was obtained from the chloride (IIIA) and potassium palladochloride. It separates as a dirty, green, micro-crystalline powder sparingly soluble in water:

0.1053 gave 0.1107 AgCl. Cl=26.06.

$\text{PtPdH}_{12}\text{O}_2\text{N}_4\text{Cl}_4$  requires Cl=26.08 per cent.

*trans-Diaminodihydroxylaminoplatinous Chloride (IIIB,*  
where  $\text{X}=\text{Cl}$ ).

This salt was prepared in the same manner as the *cis*-isomeride from the chloride of Reiset's Base II. It crystallises from hot water, in which it is readily soluble, in colourless prisms, and is precipitated from aqueous solutions by hydrochloric acid or alcohol:

0.1549 gave 0.0825 Pt. Pt=53.24.

0.0944 „ 0.0727 AgCl. Cl=19.13.

0.1930 „ 25.3 c.c.  $\text{N}_2$  at  $21^\circ$  and 773 mm. N=15.12.

$\text{PtH}_{12}\text{O}_2\text{N}_4\text{Cl}_2$  requires Pt=53.27; Cl=19.37; N=15.30 per cent.

The chlorine atoms are both completely ionised, and are precipitated by silver nitrate. The following numbers were obtained for the molecular conductivity in aqueous solution at  $25^\circ$ :

V .....	250	500	1000
$\mu$ .....	229	240	251

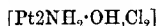
The aqueous solution is neutral towards litmus, indicating the absence of appreciable hydrolysis. By heating the chloride with hydrochloric acid on the water-bath, as mentioned above, two molecular proportions of hydroxylamine are eliminated with the formation of the chloride of Reiset's Base II. (Found: Pt=65.11. Calc.: Pt=65.11 per cent.)

The *trans*-chloride may also be obtained by the interaction of *trans*-dichlorodihydroxylaminoplatinum,  $[\text{Pt}2\text{NH}_2\cdot\text{OH}, \text{Cl}_2]$ , and ammonia.

This reaction was first studied by Alexander (*loc. cit.*), who employed four molecular proportions of ammonia and one of the chloro-compound in aqueous solution, and obtained a flocculent, reddish-white precipitate, which he regarded as the free base,  $[\text{Pt}2\text{NH}_2\cdot\text{OH}, 2\text{NH}_3](\text{OH})_2$ . By dissolving it in cold dilute hydrochloric acid, he states that the chloride,  $[\text{Pt}2\text{NH}_2\cdot\text{OH}, 2\text{NH}_3]\text{Cl}_2$ , was obtained, yielding a dark green platinochloride.

Alexander stated, further, that his chloride was precipitated by alkali hydroxides, yielding an amorphous, gelatinous mass insoluble in water. On the other hand, his chloride was very unstable towards concentrated hydrochloric acid, which decomposed it with the loss of two molecular proportions of ammonia and the formation of *trans*-dichlorodihydroxylaminoplatinum.

The properties of this substance being thus entirely different from the properties of the chloride described above, we decided to repeat the corresponding part of Alexander's work. It appeared from our experiments that, under the conditions mentioned by this author, ammonia indeed gives with the compound

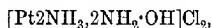


an insoluble, amorphous, pale yellow precipitate, but this is by no means formed by the addition of ammonia to dichlorodihydroxylaminoplatinum. On the contrary, its composition corresponds approximately with the formula  $[\text{PtNH}_2\cdot\text{OH},\text{Cl}(\text{OH})]$  of a hydroxo-compound, one atom of chlorine being displaced by a hydroxyl group, and, as was to be expected, we were unable to obtain from this substance the mixed chloride,



by the action of hydrochloric acid.

The addition of ammonia to the compound  $[\text{Pt}2\text{NH}_2\cdot\text{OH},\text{Cl}_2]$ , may be easily effected by using anhydrous liquid ammonia and by operating in a sealed tube. An orange solution is obtained at first, which is gradually decolorised. At the same time, a colourless, crystalline precipitate of the chloride,



separates. The composition of the substance was verified by analysis, and its identity with the *trans*-isomeride was proved by its characteristic reactions. It was specially ascertained that this chloride yielded, on heating with with hydrochloric acid, the chloride of Reiset's Base II. *trans*-Dichlorodihydroxylaminoplatinum could not be obtained under these conditions.

The *platinochloride* of the salt just described may be obtained by the addition of potassium platinochloride to its solution; it forms microscopic, dark green needles, which are sparingly soluble in cold water and may be recrystallised from hot water containing a little hydrochloric acid. It is much more stable than the *cis*-isomeride:

0.0714 gave 0.0438 Pt. Pt=61.40.

0.1335 „ 10.5 c.c.  $\text{N}_2$  (moist) at  $21^\circ$  and 773 mm. N=9.07.

$\text{Pt}_2\text{H}_{12}\text{O}_2\text{N}_4\text{Cl}_4$  requires Pt=61.75; N=8.86 per cent.

The *palladochloride*, similarly prepared by the aid of ammonium alladochloride, forms microscopic, olive-green needles:

0.0665 gave 0.0698 AgCl. Cl=26.00.

$\text{PtPdH}_{12}\text{O}_2\text{N}_4\text{Cl}_4$  requires Cl=26.08 per cent.

*trans-Dichloroamminohydroxylaminoplatinum* (VI, p. 886).

One gram of the *cis*-chloride,  $[\text{Pt}2\text{NH}_3,2\text{NH}_2\cdot\text{OH}]\text{Cl}_2$ , is heated in the water-bath for one and a-half hours with 5 c.c. of hydrochloric acid (D 1.19) and 20 c.c. of water. The colour of the solution must remain yellow; if it turns orange-red, the reaction has proceeded too far. On cooling, the mixed compound separates in characteristic aggregates of dentate yellow crystals, which may be recrystallised from very dilute hydrochloric acid. The yield is 70–90 per cent. of the theoretical:

0.0934 gave 0.0576 Pt. Pt=61.64.

0.1578 „ 12.4 c.c.  $\text{N}_2$  (moist) at  $20^\circ$  and 756 mm. N=8.91.

0.1119 „ 0.1004 AgCl. Cl=22.19.

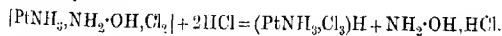
$\text{PtH}_6\text{ON}_2\text{Cl}_2$  requires Pt=61.75; N=8.76; Cl=22.43 per cent.

The substance is sparingly soluble in cold, but much more readily so in hot water, and very sparingly so in alcohol.

The aqueous solution is greenish-yellow, and immediately after the addition of silver nitrate gives only a slight opalescence, the precipitation of silver chloride occurring only gradually and being accelerated by heating.

It must accordingly be assumed that the chlorine atoms are in direct union with the platinum. This conclusion was confirmed by the determination of the molecular conductivity (in aqueous solution at  $25^\circ$ ), which gave very low values almost approaching zero:  $\mu=2.05$  ( $V=526$ ). The values of  $\mu$  rise very quickly with time, hydrolysis evidently taking place under these conditions.

By the prolonged action of hot hydrochloric acid, the substance is decomposed with the elimination of one molecular proportion of hydroxylamine and formation of the complex acid,  $[\text{PtNH}_3, \text{Cl}_3]\text{H}$ , covered by Cossa:



This acid was identified by precipitating the solution with the chloride of Reiset's Base I. The characteristic orange-yellow adratie scales of Cossa's salt,  $[\text{PtNH}_3, \text{Cl}_3]_2[\text{Pt}4\text{NH}_3]$ , were obtained, and its composition was verified by analysis. (Found: =61.92. Calc.: Pt=65.10 per cent.)

*Triamminohydroxylaminoplatinous Chloride,*  
 $[\text{Pt}(\text{NH}_3)_3, \text{NH}_2\cdot\text{OH}]\text{Cl}_2$ .

This substance was prepared by the interaction of the mixed salt just described and anhydrous liquid ammonia in a sealed tube at the ordinary temperature. After the expulsion of free ammonia, a colourless, crystalline powder remained which crystallised from 80 per cent. alcohol in colourless, glistening plates very readily soluble in water:

0.1206 gave 0.0673 Pt. Pt = 55.83.

0.0950 „ 0.0781 AgCl. Cl = 20.34.

0.1436 „ 20.1 c.c.  $\text{N}_2$  (moist) at  $21^\circ$  and 770 mm. N = 16.07.  
 $\text{PtH}_{12}\text{ON}_4\text{Cl}_2$  requires Pt = 55.73; Cl = 20.25; N = 16.00 per cent.

On heating with hydrochloric acid, the substance is decomposed, hydroxylamine being eliminated and Cleve's salt,  $[\text{Pt}3\text{NH}_3, \text{Cl}]\text{Cl}_2$ , being formed, which was detected by means of its very characteristic platinumchloride,  $[\text{Pt}3\text{NH}_3, \text{Cl}]_2\text{PtCl}_4$ .

The *platinochloride*,  $[\text{Pt}3\text{NH}_3, \text{NH}_2\cdot\text{OH}]\text{PtCl}_4$ , was obtained by precipitating the preceding chloride with potassium platinochloride, as a pale green powder consisting of microscopic needles which may be recrystallised from hot water:

0.1001 gave 0.0634 Pt. Pt = 63.34.

0.2186 „ 17.4 c.c.  $\text{N}_2$  (moist) at  $21^\circ$  and 773 mm. N = 9.17.

0.1103 „ 0.1038 AgCl. Cl = 23.28.

$\text{Pt}_2\text{H}_{12}\text{ON}_4\text{Cl}_4$  requires Pt = 63.34; N = 9.10; Cl = 23.01 per cent.

By heating this platinochloride with hydrochloric acid, hydroxylamine is eliminated, and the characteristic pink plates of Cleve's salt,  $[\text{Pt}3\text{NH}_3, \text{Cl}]_2\text{PtCl}_4$ , separate, especially on cooling, together with unchanged substance. The separation of the two can be effected by levigation and by subsequent recrystallisation from very dilute hydrochloric acid.

*Aminotrihydroxylaminoplatinous Chloride,*  
 $[\text{PtNH}_3(\text{NH}_2\cdot\text{OH})_3]\text{Cl}_2$ .

The mixed chloride,  $[\text{PtNH}_3, \text{NH}_2\cdot\text{OH}, \text{Cl}_2]$ , was gently heated with the theoretical quantity of hydroxylamine hydrochloride and the equivalent quantity of sodium hydroxide in aqueous solution. The new chloride is very readily soluble in water, and may be separated from a concentrated aqueous solution by the addition of alcohol or of hydrochloric acid. It forms transparent, colourless crystals:

0.1061 gave 0.0542 Pt. Pt=51.03.

0.1126 „ 14.4 c.c.  $N_2$  (moist) at  $19.4^\circ$  and 765.5 mm.  
N=14.68.

0.1058 gave 0.0788 AgCl. Cl=18.42.

$PtH_{12}O_2N_4Cl_2$  requires Pt=51.07; N=14.67; Cl=18.55 per cent.

The chlorine atoms are both completely ionised. The figures obtained for the molecular conductivity at  $25^\circ$  are:  $V=1000$ ;  $\mu=240$ .

The *platinochloride*, precipitated from a solution of the preceding salt by means of potassium platinochloride, forms microscopic, rose-violet needles:

0.1119 gave 0.0675 Pt. Pt=60.14.

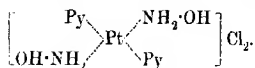
$Pt_2H_{12}O_2N_4Cl_4$  requires Pt=60.22 per cent.

The *palladochloride*, similarly obtained from ammonium palladochloride, crystallises in reddish-violet needles:

0.0567 gave 0.0587 AgCl. Cl=25.62.

$PtPdH_{12}O_2N_4Cl_4$  requires Cl=25.37 per cent.

*trans-Dipyridinodihydroxylaminoplatinous Chloride,*



This substance was prepared by the interaction of pyridine and *trans*-dichlorodihydroxylaminoplatinum. Dry pyridine readily dissolves the dichloro-compound, forming an orange-yellow solution, which loses its colour very quickly, and at the same time a colourless, crystalline powder separates. The mixture is heated or some minutes and filtered after cooling. The residue is then washed with alcohol and recrystallised from hot water:

0.0986 gave 0.0392 Pt. Pt=39.76.

0.1133 „ 0.0649 AgCl. Cl=14.1.

$C_{10}H_{16}O_2N_4Cl_2Pt$  requires Pt=39.80; Cl=14.4 per cent.

Potassium platinochloride precipitates the platinochloride,  $^{12}Py_2(NH_2 \cdot OH)_2PtCl_4$ , which crystallises in microscopic, pale prisms:

0.1450 gave 0.0746 Pt. Pt=51.41.

$C_{10}H_{16}O_2N_4Cl_4Pt_2$  requires Pt=51.61 per cent.

On heating with hydrochloric acid, *trans*-dipyridinodihydroxylaminoplatinous chloride behaves in a similar manner to the corresponding ammonia compound; the substance loses two molecular proportions of hydroxylamine and dichlorodipyridinoplatinum is

formed. (Found: Pt=45.78. Calc.: Pt=46.03 per cent.) This substance possesses all the properties assigned to it by Jørgensen (*J. pr. Chem.*, 1886, [ii], 33, 489).

#### Appendix.

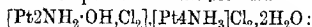
*trans*-Dichlorodihydroxyaminoplatinum (A, p. 885).

This substance, as stated by Alexander, is easily obtainable from the tetrahydroxylamine compound,  $[\text{Pt}4\text{NH}_2\cdot\text{OH}]\text{Cl}_2$ , by heating it with dilute hydrochloric acid, and separates from the solution, on cooling, in large orange needles or prisms.

In complete accordance with Werner's theory, it possesses the property of a typical non-electrolyte, for it gives only a slight opalescence immediately after the addition of silver nitrate to its aqueous solution, whilst the complete precipitation of silver chloride is effected only after a long time, but very quickly by heating. The conductivity measurements gave also, as was to be expected very low figures approaching zero:  $V=287$  ( $t=25^\circ$ );  $\mu=1.25$ .

A more thorough study of this substance showed that it has the property of forming double compounds with certain chlorides, such as the chloride of Reiset's Base I and caesium chloride.

Two grams of the compound,  $[\text{Pt}2\text{NH}_2\cdot\text{OH},\text{Cl}_2]$ , and 2 grams of the chloride,  $[\text{Pt}4\text{NH}_3]\text{Cl}_2$ , were dissolved in 6 c.c. of hot water. On cooling, the additive compound separated in well-defined, pale yellow, prismatic crystals fairly readily soluble in water, the composition of which corresponds with the formula



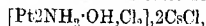
1.4070 gave 0.0722  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}=5.13$ .

0.2357 „ 0.1309 Pt. Pt=55.54.

$\text{Pt}_3\text{H}_{18}\text{O}_2\text{N}_6\text{Cl}_4\cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=5.13$ ; Pt=55.58 per cent.

The water is eliminated at  $100-110^\circ$ , but not in a vacuum desiccator over sulphuric acid (the anhydrous salt gave Pt=58.51; Calc.: Pt=58.58 per cent.).

The double compound with caesium chloride,



was obtained in a similar manner and has almost the same properties:

0.1658 gave 0.1634  $\text{Cs}_2\text{PtCl}_6$ . Cs=40.08.

0.1854 „ 0.0544 Pt. Pt=29.34.

0.1659 „ 0.1435  $\text{AgCl}$ . Cl=21.40.

$\text{PtCs}_2\text{H}_8\text{O}_2\text{N}_2\text{Cl}_4$  requires Cs=39.76; Pt=29.15; Cl=21.23 per cent.

The existence of these double compounds may be considered as an indication of the property possessed by the non-electrolyte

[Pt<sub>2</sub>NH<sub>2</sub>·OH,Cl<sub>2</sub>], of combining with two chlorine ions to yield the unstable complex anion, [Pt<sub>2</sub>NH<sub>2</sub>·OH,Cl<sub>4</sub>]<sup>7</sup>.

Accordingly, the constitution of the double compounds may be represented by the formulæ [Pt<sub>2</sub>NH<sub>2</sub>·OH,Cl<sub>4</sub>][Pt<sub>4</sub>NH<sub>3</sub>] and Pt<sub>2</sub>NH<sub>2</sub>·OH,Cl<sub>4</sub>]C<sub>8</sub>H<sub>7</sub>.

THE UNIVERSITY,  
PETROGRAD.

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### LXXXI.—*Trimorphic Change of 4-Nitroaceto-o-toluidide.*

By FREDERICK DANIEL CHATTAWAY.

CASES of trimorphic change, although several have been observed, are sufficiently rare for a new one to be of interest. The phenomenon is well shown by 4-nitroaceto-o-toluidide, which on crystallisation undergoes two successive transformations before a stable state is reached.

By nitrating *o*-toluidine in the presence of excess of concentrated sulphuric acid, Nölting and Collin (*Ber.*, 1884, **17**, 269) first prepared the base, and by heating with acetic anhydride converted it into the acetyl derivative. This they describe very briefly as crystallising in yellowish-white needles melting at 150—151°.

Speaking in general terms, all anilides crystallise in one of three easily recognisable forms, namely, a slender prismatic form, a compact form, and a hair-like form, and many have been obtained in two of them.

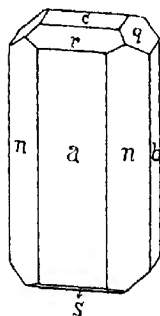
4-Nitroaceto-o-toluidide can be obtained in all three forms, the order of stability being: slender prismatic → compact → hair-like.

It is moderately readily soluble in boiling alcohol, giving a pale yellow solution, from which very slender prisms of the first, or α-form, separate on cooling. These are of such a pale yellow colour that when dry they appear almost colourless. If the original solution is sufficiently concentrated, they grow until the whole liquid is filled with a mass of slender crystals, generally radiating from a few points. If these crystals are allowed to remain in the mother liquor at the ordinary temperature, small, yellow, six-sided plates of the second, or β-modification, soon make their appearance, and rapidly grow at the expense of the first form, which dissolves in their neighbourhood, forming cavities occupied by one or more crystals that may increase to a considerable size



and are usually well shaped. The transformation into the second form is generally complete after the lapse of a few days if the beaker is left undisturbed, although the time taken depends greatly on the average temperature, and is much shortened by occasionally shaking the transforming mass. When the change is complete, a relatively thin layer of well-shaped, compact crystals remains at the bottom of the beaker.

After some time, often before complete transformation of the first into the second form, a third, or  $\gamma$ -modification, makes its appearance in tufts of colourless, hair-like crystals resembling small colonies of a mould or tiny balls of cotton wool. These increase in size, the compact form dissolving and disappearing until the whole contents of the beaker become a felted mass having a superficial resemblance to a somewhat slimy jelly. From this, the mother



liquor is removed only with difficulty by filtration or pressure. Direct transformation of the  $\alpha$ - into the  $\gamma$ -form occurs if the mass of slender prismatic crystals first separating is seeded with a few crystals of the hair-like form.

All three forms, when heated, soften and melt at the same temperature, namely,  $150-151^{\circ}$ , which seems to indicate that before the fusion point is reached transformation into the form most stable near that temperature takes place.

Mr. T. V. Barker, who has very kindly examined the crystals, reports on them as follows.

The first, or  $\alpha$ -modification, crystallises in doubly refracting needles with straight extinction.

The well-developed crystals of the  $\beta$ -modification belong to the monoclinic system. Forms:  $a(100)$ ,  $c(001)$ ,  $n(210)$ ,  $b(010)$ ,  $q(011)$  and  $r(101)$ ; also, occasionally,  $s(\bar{1}01)$ , and, very rarely,  $x(021)$  and

$p(012)$ . The general habit and common forms of the crystals are shown in the figure. Crystallographic constants:  $57^{\circ}26'$ ,  $a(48^{\circ}34')m(41^{\circ}26')b$ ,  $49^{\circ}43'$ ,  $74^{\circ}10'$ , or, alternatively,  $a:b:c=1:178:1:0.6388$ ,  $\beta=105^{\circ}50'$ . Three crystals were measured on the two-circle goniometer; following are the mean values of the most trustworthy results:

	$b(010)$ .	$a(100)$ .	$n(210)$ .	$c(001)$
Azimuth .....	Face of	$0^{\circ} 0'$	$0^{\circ} 0'$	$*74^{\circ} 10'$
Polar distance ...	reference	$90 0$	$*60 28$	$90 0$

	$q(011)$ .	$r(101)$ .	
Azimuth .....	$74^{\circ} 10'$	$50^{\circ} 13'$	(calc. = $49^{\circ} 43'$ )
Polar distance ...	$*58 25\frac{1}{2}$	$90 0$	

Optically, biaxial; axial plane,  $b(010)$ ; extinction on  $b(010)$ ,  $37^{\circ}$  with prism edge in the obtuse angle  $\beta$ . Complex-symbol:  $k; +16/42/+3\frac{1}{2}$ .

The third, or  $\gamma$ -modification, crystallises in hair-like, doubly refracting needles with an extinction of  $35^{\circ}$ .

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[Received, October 21st, 1918.]

## XXXII.—The Preparation of Ethylamine and of Diethylamine.

By EMIL ALPHONSE WERNER.

IN the preparation of ethylamine and of diethylamine by the interaction of ethyl bromide and ammonia, it has been the usual practice, so far as hitherto recorded, to submit the whole of the alkyl haloid to the action of ammonia in a single operation.

This is a faulty procedure, since it conduces largely to the formation of the less useful triethylamine, with consequent loss in the yields of the primary and secondary bases. Whether the change promoted by heat or is allowed to proceed at the ordinary temperature, the tertiary amine has been present in largest amount in the final product (compare Garner and Tyrer, T., 1916, 109, 4).

The author has found that when ethylamine is added to an alcoholic solution of diethylammonium chloride, the displacement of the secondary amine by the primary is quantitative; thus

diethylamine only was obtained on distillation of the mixture after it had remained for an hour, whilst under similar conditions the displacement of triethylamine from its hydrochloride by diethylamine was likewise quantitative (Expts. I, II).

A fair separation of all three amines, in the same order, has been effected by fractional treatment of a solution of their salts with sodium hydroxide; the tertiary amine was first liberated, the secondary next, and the primary amine last (Expt. III).

It must be admitted that these results go to show, contrary to the commonly accepted view, that triethylamine is the weakest base of the three amines.

Reasoning on this basis, and bearing in mind the relative tendency to dissociation\* of the respective 'amine' salts, a procedure has been adopted whereby the formation of triethylamine has been almost completely suppressed. Thus, from the product of two experiments, in which 2090 grams of ethyl bromide were used, only 27 grams of triethylamine were obtained, whilst the yield of ethylamine was 33.8 per cent. and of diethylamine 57.5 per cent. of the theoretical.

The influence of the proportion of ammonia to ethyl bromide on the yield of ethylamine is shown by the following results:

Molecular ratio					
EtBr : $\text{NH}_3$ .....	1:1	1:4	1:6	1:8	1:16
Percentage yield of $\text{NH}_2\text{Et}$ on theoretical .....	11.3	24.4	26.7	28.1	34.2

The necessity of maintaining a good excess of ammonia throughout the progress of the reaction is indicated by theory.

#### EXPERIMENTAL.

##### *Preparation of Ethylamine and of Diethylamine.*

Five litres of 90 per cent. alcohol were saturated with ammonia (compare this vol., p. 698) until 490 grams of the gas had been dissolved, 200 grams of ethyl bromide were added (ratio EtBr to  $\text{NH}_3$  approximately 1 to 16), after which, at successive intervals of two days, fresh quantities of the alkyl haloid were added in the following amounts: 180, 170, 150, 130, 110, 100, 80, and, finally 66 grams. Preliminary experiments had shown that with the above ratio of ammonia the whole of the ethyl bromide was decomposed after two days, hence the successive quantities were regulated

\* The term as used here does not refer to ionisation or electrolytic dissociation.

so as to maintain the desired excess of ammonia throughout the progress of the change. In all, 1186 grams of ethyl bromide were used; ammonium bromide began to separate on the twelfth day, and on the sixteenth day the preparation was stopped. Test experiments on a small scale with pure alcohol had shown that when ammonium bromide separated in quantity in the early stage of the process, the formation of triethylamine was promoted when the reaction was prolonged. The reason is fairly obvious when the probable mechanism of the process is considered, hence it was found advantageous to use alcohol containing 10 per cent. of water.

The alcoholic solution, separated from ammonium bromide, was concentrated by distillation (the ammonia evolved was used to charge more alcohol) until nearly all the ammonium bromide formed had separated, 362 grams of which were recovered.

The solution of the hydrobromides of the mixed amines was distilled until the temperature reached  $130^{\circ}$ , in order to remove the last traces of alcohol. Where it was not found convenient to liberate the entire quantity of the mixed amines by the addition of aqueous sodium hydroxide to the residue, chloroform was used as a solvent for their separation.

Ethylammonium bromide is dissolved by chloroform to the extent of only 0.163 gram in 100 c.c. at  $14^{\circ}$ , whilst the same volume of chloroform dissolves 42 grams of diethylammonium bromide. By this means, 465 grams of pure ethylammonium bromide and 510 grams of diethylammonium bromide, containing slightly more than 5 per cent. of triethylammonium bromide, were obtained. After the separation of triethylamine (14 grams) by treatment with the requisite proportion of sodium hydroxide, 226 grams of diethylamine, collected at  $56-57.5^{\circ}$  and dried over potassium hydroxide, were obtained.

(a) *Displacement of Diethylamine by Ethylamine, and of*  
(b) *Triethylamine by Diethylamine.*

*Expt. I.*—(a) Nine grams of pure ethylamine were added to 12 grams of diethylammonium chloride dissolved in 30 c.c. of alcohol. After an hour, all free amine was removed by distillation. The hydrochloride prepared from the distillate gave  $\text{Cl}=32.33$ , whilst  $\text{NH}_4\text{Et}_2\text{HCl}$  requires  $\text{Cl}=32.42$  per cent. The displacement of the secondary amine from its salt was therefore complete.

*Expt. II.*—(b) Eight grams of pure diethylamine were added to 15 grams of triethylammonium chloride dissolved in 35 c.c. of

## 902 THE PREPARATION OF ETHYLAMINE AND OF DIETHYLAMINE.

alcohol. The mixture was distilled as in the previous experiment. The hydrochloride prepared from the distillate gave  $\text{Cl}=25.78$ , whilst  $\text{NEt}_3\text{HCl}$  requires  $\text{Cl}=25.81$  per cent. The displacement of the tertiary amine by the secondary was therefore complete.

### *Separation of the Three Amines by Sodium Hydroxide.*

*Expt. III.*—To a solution which contained 13.8 grams of triethylammonium chloride, 11 grams of diethylammonium chloride, and 9 grams of ethylammonium chloride dissolved in 60 c.c. of water, 4 grams of sodium hydroxide were added. The solution was well shaken, and after twenty hours the liberated amine was distilled off.

The hydrochloride prepared from it gave  $\text{Cl}=26.04$ , whilst  $\text{NEt}_3\text{HCl}$  requires  $\text{Cl}=25.81$  per cent. The amine was therefore almost pure triethylamine.

To the remaining solution, when cold, 4 grams of sodium hydroxide were added, and a similar treatment was applied.

The hydrochloride prepared from the liberated amine gave  $\text{Cl}=34.44$ , which corresponds with a mixture, in round numbers, of diethylamine=85 and ethylamine=15 per cent. The residual solution was directly distilled after a final addition of sodium hydroxide. The hydrochloride prepared from the distillate gave  $\text{Cl}=41.12$ ; the liberated amine had, therefore, the approximate composition, ethylamine=75 and diethylamine=25 per cent. These results indicate that this method of procedure for the separation of the amines may prove useful on a larger scale, and the subject is under investigation in connexion with certain of the higher aliphatic amines.

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[Received, October 8th, 1918.]

## Organic Chemistry.

**Two New Trihydric Alcohols.** MORITZ KOHN and VIKTOR NEUSTÄDTER (*Monatsh.*, 1918, **39**, 293-298).—It has already been found possible (Kohn, A., 1914, i, 74) by the action of magnesium methyl iodide on the lactone of  $\alpha\gamma$ -dihydroxy- $\alpha\gamma$ -dimethyl-*n*-valeric acid to obtain  $\beta\gamma$ -trihydroxy- $\beta\gamma$ -trimethyl-*n*-hexane. Formisobutyraldol, by successive treatment with sodium hydrogen sulphite and potassium cyanide (compare Glaser, A., 1904, i, 284), can be converted into the lactone of  $\alpha\gamma$ -dihydroxy- $\beta\beta$ -dimethyl-*n*-butyric acid, b. p. 118–120°/12 mm., 237–241°/ord. pressure, which reacts with magnesium methyl iodide in a similar manner to the above compound, forming  $\alpha\gamma\delta$ -trihydroxy- $\beta\beta\delta$ -trimethyl-*n*-pentane,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$ , b. p. 152–155°/12 mm., 256–262°/ord. pressure, which slowly solidifies to a crystalline mass, m. p. 68–70°. When heated with 33% sulphuric acid, this compound yields a substance,  $\text{C}_9\text{H}_{16}\text{O}_2$ , b. p. 187–192°, of camphor-like odour, probably 4-hydroxy-3:3:5:5-tetramethyltetrahydrofuran,  $\begin{array}{c} \text{CH}_2\cdot\text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CMe}_2 \end{array} > \text{CH}\cdot\text{OH}$ . The action of magnesium phenyl bromide on the lactone proceeds in an analogous manner, and yields  $\alpha\gamma\delta$ -trihydroxy- $\beta\beta$ -diphenyl- $\beta\beta$ -dimethyl-*n*-butane, microscopic needles, m. p. 130–133°. D. F. T.

**Action of Phosphorus Trichloride on Aliphatic Alcohols.** T. MIŁOBENDZKI and A. SACHNOWSKI (*Chemik Polski*, 1917, **15**, 34–37; from *Chem. Zentr.*, 1918, i, 911–912).—The action of phosphorus trichloride on any alcohol results in the immediate formation of the normal ester of phosphorous acid, which is decomposed by the liberated hydrogen chloride into acid ester and alkyl chloride,  $\text{PCl}_3 + 3\text{R}\cdot\text{OH} = \text{P}(\text{OR})_3 + 3\text{HCl} \rightarrow \text{OH}\cdot\text{P}(\text{OR})_2 + \text{RCl} \rightarrow \text{OR}\cdot\text{P}(\text{OH})_2 \rightarrow \text{P}(\text{OH})_3 + \text{RCl}$ . The decomposition of alkyl phosphites into phosphorous acid and unsaturated hydrocarbons is a secondary reaction which occurs most readily with esters derived from tertiary alcohols (even at low temperature and under diminished pressure).

The authors have demonstrated that the reaction for the diagnosis of isomeric alcohols (action of dry hydrogen chloride on the alkyl phosphites) proceeds quantitatively and is not merely a qualitative test.

For the preparation of normal esters, the following method is recommended. The mixture of alcohol (3 mols.) and pyridine (3 mols.) is largely diluted with ether, and phosphorus trichloride (1 moi.) is added drop by drop to the ice-cold mixture. The precipitated pyridine hydrochloride is filtered. The following yields were obtained: trimethyl phosphite, b. p. 110–111.5°/745 mm.

(crude product, 70%; pure substance, 42.5%); triethyl phosphite, b. p. 155–156°/740 mm. (73%); tri-*n*-propyl phosphite, b. p. 82–84°/10 mm. (89%); tri-*n*-butyl phosphite, b. p. 122–123°, 12 mm.,  $D_4^{20}$  0.92547,  $D_4^{25}$  0.92530,  $D_4^{30}$  0.92692 (96%).

Dialkyl phosphites are prepared by a similar method, except that only two molecules of pyridine are used for each molecule of phosphorus trichloride. The details are as follows: dimethyl hydrogen phosphite, b. p. 56–58°/10 mm. (ca. 35%); diethyl hydrogen phosphite, b. p. 72–73°/9 mm. (85%); di-*n*-propyl hydrogen phosphite, b. p. 91–92°/10 mm. (96%); di-*n*-butyl hydrogen phosphite, b. p. 124–125°/12 mm.,  $D_4^{20}$  0.99516,  $D_4^{25}$  0.99503,  $D_4^{30}$  0.99697 (97%).

Attempts have been made to prepare mono-alkyl phosphites by the action of phosphorus trichloride on the alcohols saturated with hydrogen chloride; a relationship between the product of the reaction and the degree of saturation of the alcohol has been traced, but this section of the work has not been completed.

The reaction between phosphorus trichloride and trimethylcarbinol has been similarly investigated. The formation of unsaturated hydrocarbons and of trimethylcarbinyl chloride is not observed during the action when three molecules of pyridine are used for each molecule of phosphorus chloride. The product, the composition of which corresponded fairly accurately with that required for  $(C_3H_7O)_3P$ , could not be distilled without decomposition, whereby diisobutylene, b. p. 102–103°/758 mm., triisobutylene, b. p. 178–180°/752 mm., together with unchanged tributyl phosphite, were obtained. Di-*tert*-butyl hydrogen phosphite is still more readily decomposed, yielding at 38° (30 mm.) di- and triisobutylene.  
H. W.

**Action of Water on Dialkyl Phosphites.** T. MILOBENDZKI and A. SACHNOWSKI (*Chemik Polski*, 1917, 15, 48–55; from *Chem. Zentr.*, 1918, i, 912–913. Compare Milobendzki, A., 1912, i, 155).—The stability of dialkyl phosphites in aqueous solution and their electrical conductivity have been investigated. Hydrolysis of the esters,  $OH \cdot P(OR)_2$ , with alkali or barium hydroxide in solutions which are not below 0.05*N* proceeds too rapidly for accurate measurement. The hydrolysis of the esters proceeds slowly in aqueous solution at 25°; measurements have been made for diethyl hydrogen phosphite and dipropyl hydrogen phosphite, for full details of which the original paper must be consulted. The velocity of hydrolysis is very high at first, then decreases, subsequently increases, and finally sinks.

The dialkyl hydrogen phosphites behave as neutral substances. They do not combine with ammonia even when nascent; their aqueous solutions are neutral to indicators. The conductivity of the aqueous solutions is small—about ten times that of the water. The electrical conductivity of an equimolecular mixture of dipropyl hydrogen phosphite and silver nitrate is less than the sum of their conductivities. In the first thirty to forty minutes, no reaction

appears to occur; subsequently, the silver salt,  $\text{OAg}\cdot\text{P}(\text{OPr})_2$ , slowly commences to separate, but precipitation is not complete after forty hours. The silver salt is stable beneath the aqueous solution in the dark and does not begin to decompose for about forty hours.

H. W.

**Salts of Alkyl Hydrogen Phosphites.** T. MIŁOBENDZKI and MARIE SZWEJKOWSKA (*Chemik Polski*, 1917, 15, 56—65; from *Chem. Zentr.*, 1918, i, 913—914).—Barium monoalkylphosphites are prepared by the neutralisation of monoalkylphosphorous acids or the hydrolysis of dialkyl hydrogen phosphites. Barium ethyl hydrogen phosphite,  $\text{Ba}[\text{O}\cdot\text{P}(\text{OEt})\cdot\text{OH}]_2$ , forms hygroscopic crystals; it is completely hydrolysed in warm aqueous solution. Barium isopropyl hydrogen phosphite is similar. Ferric propyl hydrogen phosphite, obtained by the action of ferric hydroxide on an excess of the ester in concentrated aqueous solution or by precipitation of the solution of the barium salt by ferric chloride, is very sparingly soluble in water. It is very slowly attacked by ammonia, rather more rapidly by dilute acids, but is only slowly soluble even in fuming hydrochloric acid. Ferric isopropyl hydrogen phosphite resembles the *n*-propyl salt. The ferric isobutyl and isoamyl hydrogen phosphites are similarly prepared. The monomethyl and monoethyl phosphites could not be obtained by precipitation. Cuprous dialkyl phosphites,  $(\text{OR})_2\text{P}\cdot\text{OCu}$ , are obtained when cuprous oxide acts on an aqueous solution of excess of the ester in closed vessels. The reaction,  $(\text{OR})_2\text{P}\cdot\text{OH} + \text{CuOH} \rightarrow (\text{OR})_2\text{P}\cdot\text{OCu} + \text{H}_2\text{O}$ , proceeds slowly and is complete in five days; simultaneously, the white cuprous salt is slowly oxidised to the blue cupric salt, copper being precipitated. Purification is effected by pouring the product into water, when the copper and copper oxide sink, the cupric salt passes into solution, and the cuprous salt collects on the sides of the vessel. The dry salts are stable. The cuprous salts of diethyl, dipropyl, and diisopropyl hydrogen phosphites are described. The silver salts of the dialkyl phosphites are obtained by the cautious addition of alkali or of a solution of a readily hydrolysed salt to an aqueous solution of equivalent quantities of silver nitrate and the requisite ester, or, preferably, by treatment of the solution of the dialkyl phosphite with ammoniacal silver nitrate and immediate neutralisation of the ammonia with nitric acid. The ester suffers a certain amount of hydrolysis, which is less marked when the second of the above methods is adopted. The silver salts are sparingly soluble in water, soluble in ammonia and alkalis. The diethyl and dipropyl salts have been particularly investigated.

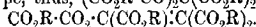
H. W.

**Constitution of Dioxalomalonic Ester and other Acylated Esters.** KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1918, 51, 1087—1106. Compare A., 1917, i, 627).—The discovery that the so-called "ethyl diacetylmalonate,"  $\text{CAc}_2(\text{CO}_2\text{Et})_2$ , is really to be regarded as ethyl  $\beta$ -acetoxyethylidenemalonate,

a a 2



$\text{OAc} \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et})_2$ , raises the question whether genuine diacylmalonic esters can be obtained at all, and whether they may not perhaps be present in small quantities in specimens of the isomeric esters. In the case of the "dioxalomalonates," Scholl and Egerer (A., 1913, i, 588) have already considered the two alternatives, analogous with the above, and decided on a formula of the true diacylmalonate type, thus,  $(\text{CO}_2\text{R} \cdot \text{CO})_2\text{C}(\text{CO}_2\text{R})_2$ , and not



Their decision depended chiefly on the facts that the compounds in question did not immediately reduce alkaline permanganate and gave carbon monoxide on heating, but it is now shown that these arguments have no weight and that the optical properties of the esters agree with the alternative formula. The refractions and dispersions are abnormally high and agree with the enolic structure rather than with the methanetetra-carboxylate type. Furthermore, "ethyl oxalomalonate" is found by titration to exist to the extent of 60% in the enolic form,  $\text{CO}_2\text{Et} \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{CO}_2\text{Et})_2$ .

These results support the opinion, often expressed by Claisen, that compounds of the type  $\text{C}(\text{CO})_4$  do not, generally speaking, exist, but tend to undergo rearrangement into isomerides in which at least one carbonyl group is attached to oxygen. There are exceptions to this generalisation, however. Scholl and Egerer's methanetetra-carboxylates and acetylmethanetricarboxylates have optical properties which agree with the type  $\text{C}(\text{CO})_4$ . The latter esters are obtained by acetylating the sodiummethanetricarboxylates, and it appears that compounds of the above type can only be obtained from methanetricarboxylates, for if the alternative procedure is adopted, namely, acetylation of malonic esters, followed by treatment with chloroformic esters, the products are the enolic isomerides.

With the co-operation of Scholl and Egerer, the optical properties of pure specimens of their methanecarboxylates have been investigated. Ethyl methanetricarboxylate has b. p.  $139^\circ/14$  mm., m. p.  $27-29^\circ$ ,  $D^{20}_D$  1.1091,  $n_D$  1.42628,  $n_D$  1.42828,  $n_D$  1.43392,  $n_D$  1.43838, at  $14.2^\circ$ ,  $E\Sigma_0 + 0.24$ ,  $E\Sigma_0 + 0.21$ ,  $E\Sigma_0 - \Sigma_0 + 2\%$ ,  $E\Sigma_0 - \Sigma_0 + 1\%$ . Ethyl methanetetra-carboxylate has b. p.  $185^\circ/18$  mm.,  $D^{20}_D$  1.1351,  $n_D$  1.43300,  $n_D$  1.43563,  $n_D$  1.44085,  $n_D$  1.44561, at  $17^\circ$ ,  $E\Sigma_0$  0.36,  $E\Sigma_0 - \Sigma_0$ , 3%,  $E\Sigma_0 - \Sigma_0$ , 4%. Dimethyl diethyl methanetricarboxylate has  $D^{20}_D$  1.1828,  $n_D$  1.43098,  $n_D$  1.43327,  $n_D$  1.43891,  $n_D$  1.44350, at  $17.2^\circ$ ,  $E\Sigma_0$  0.39,  $E\Sigma_0$  0.40,  $E\Sigma_0 - \Sigma_0$ , 5%,  $E\Sigma_0 - \Sigma_0$ , 2%. Ethyl acetylmethanetricarboxylate,  $\text{CAc}(\text{CO}_2\text{Et})_3$ , has b. p.  $263^\circ/\text{atm}$ ,  $154^\circ/11$  mm.,  $D^{20}_D$  1.1277,  $n_D$  1.43354,  $n_D$  1.43562,  $n_D$  1.44158,  $n_D$  1.44638, at  $13.1^\circ$ ,  $E\Sigma_0$  0.37,  $E\Sigma_0$  0.35,  $E\Sigma_0 - \Sigma_0$ , 5%,  $E\Sigma_0 - \Sigma_0$ , 4%, and is decomposed by phenylhydrazine and aniline in the cold, phenylhydrazide and acetanilide being deposited.

These data show that the refraction and dispersion of the tetra-carboxylates are somewhat abnormal, which might be expected of compounds with so many carbonyl groups in close proximity, but the abnormality is by no means of the same order as that revealed by enolic compounds. For example, ethyl  $\beta$ -ethylcarbonatoacrylate

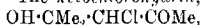
*idenemalonate*,  $\text{CO}_2\text{Et}\cdot\text{O}\cdot\text{CMe}_2\cdot\text{C}(\text{CO}_2\text{Et})_2$ , the isomeride of ethyl acetylmethanetricarboxylate, which is prepared by the action of ethyl chloroformate on "ethyl acetylmalonate" in the presence of pyridine, or on the sodium compound of this ester, is a colourless oil with b. p.  $166^\circ/12$  mm.,  $D_4^{15.4}$  1.1330,  $n_D$  1.44821,  $n_D$  1.45084,  $n_D$  1.45835,  $n_D$  1.46441, at  $13.4^\circ$ ,  $E\sum_s$  0.50,  $E\sum_D$  0.51,  $E\sum_s - \sum_s$  19%,  $E\sum_s - \sum_s$  19%. Scholl's ethyl oxalomethanetricarboxylate [ethyl  $\beta$ -ketoethane- $\alpha\alpha\beta$ -tetracarboxylate],  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Et})_2$ , is likewise not unduly abnormal; it has b. p.  $201\text{--}202^\circ/23$  mm.,  $D_4^{15.4}$  1.1671,  $n_D$  1.43820,  $n_D$  1.44026,  $n_D$  1.44627, at  $15.15^\circ$ ,  $E\sum_s$  0.48,  $E\sum_D$  0.46,  $E\sum_s - \sum_s$  7%.

For the preparation of ethyl "oxalomalonate" and "dioxalomalonate," absolutely pure ethyl oxalyl chloride is essential, and the authors have found that the best method of preparation is that described by Diels and Nawiasky (A., 1904, i, 981). Ethyl "oxalomalonate" exists to the extent of about 61% as the enol.

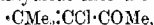
$\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})_2 \rightleftharpoons \text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{CO}_2\text{Et})_2$ , and has  $D_4^{15.2}$  1.1546,  $n_D$  1.44514,  $n_D$  1.44794,  $n_D$  1.45562,  $n_D$  1.46229, at  $15.2^\circ$ ,  $E\sum_s$  0.47,  $E\sum_D$  0.48,  $E\sum_s - \sum_s$  25%,  $E\sum_s - \sum_s$  27%, calculated for the enolic modification. Ethyl "dioxalomalonate" is in reality ethyl  $\beta$ -ethyloxalatoethylene- $\alpha\alpha\beta$ -tricarboxylate.

$\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{O}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}_2\text{Et})_2$ , and has  $D_4^{15.9}$  1.1926,  $n_D$  1.45378,  $n_D$  1.45665,  $n_D$  1.46452,  $n_D$  1.47138, at  $14.9^\circ$ ,  $E\sum_s$  0.83,  $E\sum_D$  0.84,  $E\sum_s - \sum_s$  27%,  $E\sum_s - \sum_s + 29\%$ , and yields carbon monoxide, quantitatively, when heated. J. C. W.

**Action of Hypochlorous Acid on Mesityl Oxide.** K. SŁAWIŃSKI (*Chemik Polski*, 1917, 15, 106--110; from *Chem. Zentr.*, 1918, i, 915).—The *keto*chlorohydrin,



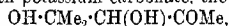
is obtained as a colourless oil which rapidly becomes red, violet, and finally brown with separation of water when a 1% solution of sodium hypochlorite is added to mesityl oxide dissolved in acetic acid; when 1 gram-mol. of hypochlorous acid is used, only 40% of the chlorohydrin is produced, but the yield may be increased to 60% by employing a 15--20% excess of hypochlorous acid. The chlorohydrin has b. p.  $96\text{--}98^\circ/32$  mm.,  $D_4^{15}$  1.1452,  $D_4^{15}$  1.1089. It is converted by acetic anhydride into the *chloroketone*,



b. p.  $55\text{--}60^\circ/20$  mm. The *keto*chlorohydrin dissolves completely in 20% potassium carbonate solution in the course of a few days, and the product of the reaction consists almost entirely of the

*keto-oxide*,  $\text{O} < \overset{\text{CMe}_2}{\text{CH}}\cdot\text{COMe}$ , a pale yellow oil of unpleasant odour,

b. p.  $54\text{--}55^\circ/15$  mm.,  $D_4^{15}$  0.9749. When a 10% aqueous solution of the *keto-oxide* is treated with one drop of hydrochloric acid and then neutralised with potassium carbonate, the compound,

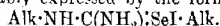


is formed as an oil, b. p.  $99\text{--}100^\circ/12$  mm., which reduces Fehling's solution in the cold; it does not give crystalline derivatives with

phenylhydrazine or semicarbazide. The dibenzoyl compound has m. p. 112—113°. H. W.

**Preparation of Alkylselenocarbamides.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P., 305262; from *Chem. Zentr.*, 1918, i, 976).—Alkylselenocarbamides are prepared by the action of hydrogen selenide on alkylcyanamides. The substances have a therapeutic value in the treatment of cancerous disease, and serve as intermediate products in the production of the more stable alkyl haloid additive compounds. *Allylselenocarbamide* forms almost colourless needles, m. p. 93°, which become superficially red owing to the separation of selenium; it unites with bromine and iodine and reduces alkaline permanganate. It is very sensitive to air and light. The mercury and lead salts eliminate selenium. *Ethylselenocarbamide* forms colourless needles, m. p. ca. 125°. H. W.

**Preparation of Derivatives of Alkylselenocarbamides.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P., 305263; from *Chem. Zentr.*, 1918, i, 976).—The alkylselenocarbamides combine readily with alkyl haloids to yield compounds in which the selenium is more firmly combined than in the parent selenocarbamides; they are more stable towards light and more soluble in water. Their composition is probably expressed by the formula



The compound formed from allylselenocarbamide and ethyl iodide forms white leaflets, m. p. about 100°; the iodine is precipitated as silver iodide by silver nitrate. The selenium is not precipitated as lead or mercury selenide by lead or mercury salts, as in the case of allylselenocarbamide. The compound from ethylselenocarbamide and allyl bromide has m. p. 115°. H. W.

**Acetyl Cyanide.** ROLAND SCHOLL [with JOSEF ADLER] (*Monatsh.*, 1918, 39, 240).—Acetyl cyanide is conveniently prepared by boiling a solution of oximinoacetone in carbon disulphide with a little more than the theoretical quantity of phosphorus pentoxide for three-quarters of an hour and then distilling; the yield is approximately 40%. D. F. T.

**Organic Chemical Reagents. I. Dimethylglyoxime.** ROGER ADAMS and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1918, 40, 1281—1289).—Methods of manufacturing the less common organic chemicals are being thoroughly worked out at the University of Illinois, and full details of the processes will be published with the object of inducing manufacturers to take up the production of the more useful of such reagents.

The present communication deals with the manufacture of dimethylglyoxime. This substance can be made by several methods, but the only one that is easily and cheaply adapted for large scale production is that of Gandurin (*A.*, 1908, i, 400). The paper describes (1) the preparation of hydroxylamine sulphate and

(2) of amyl nitrite, (3) methyl ethyl ketone, (4) the preparation of its oximino-derivative and (5) of dimethylglyoxime, (6) the purification of coloured dimethylglyoxime, and (7) the recrystallisation of dimethylglyoxime.

The removal of coloured impurities in dimethylglyoxime is effected by treating its saturated solution in 8% sodium hydroxide solution with an excess of concentrated ammonium chloride solution; the colourless precipitate of dimethylglyoxime is filtered immediately. The process is repeated if necessary. C. S.

#### Action of Magnesium and Zinc on Dichloromethylarsine.

ENRIQUE V. ZAPPI (*Bull. Soc. chim.*, 1918, [iv], 23, 322—324).—In the presence of anhydrous ether, magnesium does not act on dichloromethylarsine, but in the presence of water the two react violently, giving methylarsine, hydrogen, and methane, methylarsenide,  $(\text{CH}_3\text{As})_2$ , being precipitated and magnesium chloride left in solution. Zinc produces a similar decomposition. W. G.

#### Hydrocarbo-bases and a Study of Organic Derivatives of Mercury and of Lead.

LAUDER W. JONES and LOUIS WERNER (*Amer. Chem. Soc.*, 1918, 40, 1257—1275).—Hydrides of metals and organo-metallic compounds react with acids and suppress hydrogen ions; for example, (1)  $\text{NaH} + \text{HX} = \text{NaX} + \text{H}_2$ , (2)  $\text{Zn}(\text{CH}_3)_2 + 2\text{HX} = \text{ZnX}_2 + 2\text{CH}_4$ . If this property is sufficient reason for classifying these substances as bases, the former may be termed hydrogen bases and the latter hydrocarbo-bases. When compared with aquo-bases (KOH) and ammonio-bases ( $\text{KNH}_2$ ), the striking resemblance in chemical behaviour of these substances towards hydrogen ions seems to demand some factor common to all as the cause of the analogy, and the authors endeavour to find this factor in the theory of the electron conception of valency and Lewis's theory of electromers (*A.*, 1911, i, 431). The most obvious explanation of the similar reactivity of these various classes of bases would be to consider all groups combined with the metallic atoms as these compounds negative in the electronic sense. Whilst the organo-metallic compounds resemble aquo-bases and ammonio-bases in certain other respects, as, for example, in forming basic salts and in undergoing double decomposition in reactions, they and the hydrogen bases differ from these in one important respect—they are powerful reducing agents. This property is explained by the powerful tendency of negative hydrogen to become positively charged and of negative alkyl groups (or of a carbon atom in them) to lose negative electrons and to assume positive charges.

Mercury diethyl is known to dissociate at about  $200^\circ$  to give mercury and butane. The dissociation, considered electronically, implies that one of the alkyl groups functions negatively and the other positively.  $\text{Hg}^- + \text{Et}^+ \rightarrow \text{Hg} + \text{Et}^+ \cdot \text{Et}$ . Such groups should therefore exhibit differences in chemical reactivity, and this is

shown to be the case. Oxidation with permanganate removes only one group,  $R \cdot Hg \cdot OH$  being formed, and mercury dibenzyl, heated with glacial acetic acid at  $160-170^\circ$ , yields mercury, toluene, and benzyl acetate, together with some dibenzyl. Benzyl mercuriacetate under the same conditions gives only mercury and benzyl acetate, toluene and dibenzyl not being formed. Similar results are obtained with mercury diethyl and mercury *diisoamyl*, mercury ethane or pentane, and ethyl or *isoamyl* acetate being obtained. Mercury diphenyl and mercury dimethyl give mercury and hydrocarbons, the acetate of the phenol or alcohol not being formed.

Similarly, tetra-alkyl lead compounds react as though three of the alkyl groups were negative and the fourth positive. Thus, lead tetraethyl heated with glacial acetic acid at  $250-260^\circ$  gave lead acetate, ethane (in amount corresponding with three ethyl groups), and ethyl acetate. Results of the same kind were obtained with lead tetramethyl.

C. S.

**Dibromopyranthrone and Attempts to Prepare Benzanthrones.** ROLAND SCHOLL (*Monatsh.*, 1918, **39**, 231—236).—[With W. NEUBERGER.]—The substance obtained from pyranthrone by the action of bromine at  $100^\circ$  is a *dibromo*-compound,  $C_{31}H_{21}O_5Br_2$ .

[With W. TRITSCH.]—2-Iodo-1-methylnaphthalene,  $C_{11}H_9I$ , pearly leaflets, m. p.  $51.5^\circ$ , prepared from 1-methyl-2-naphthylamine by the diazo-reaction, when heated with finely divided copper at  $220-260^\circ$  undergoes conversion into 1:1'-dimethyl-2:2'-dinaphthyl,  $C_{22}H_{18}$ , colourless needles, m. p.  $230^\circ$ . The corresponding *dibenzyl*-2:2'-dinaphthyl,  $C_{34}H_{26}$ , and *di-p-chlorobenzyl*-2:2'-dinaphthyl,  $C_{34}H_{24}Cl_2$ , obtained by heating benzyl chloride and *p*-chlorobenzyl chloride, respectively, with 2:2'-dinaphthyl in the presence of zinc chloride, were not pure substances.

D. F. T.

**2-Methylantracene.** ROLAND SCHOLL [with JOS. LENOX] (*Monatsh.*, 1918, **39**, 237—238).—2-Methylantracene,  $C_{17}H_{14}$ , m. p.  $206-207^\circ$ , can be obtained by the action of hydriodic acid and phosphorus on 2-methylantraquinone.

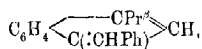
D. F. T.

**Derivatives of Fulvene. V. Condensation of Indenes with Ketones.** JOHANNES THIELE and KARL MERCK (*Annalen*, 1918, **415**, 257—273. Compare *A.*, 1906, i, 569, 571, 586, 639).—The reactivity of the methylene group in cyclopentadiene, indene, and fluorene decreases as the ethylenic linkings of the 5-ring become double linkings in a benzene nucleus. It has already been shown (*loc. cit.*) that cyclopentadiene condenses extraordinarily easily with ketones, whilst fluorene does not condense at all under the influence of alkaline condensing agents. The behaviour of indene has now been examined. It condenses easily with acetone in the presence of methyl-alcoholic potassium hydroxide, yielding, after boiling for two hours, dimethylbenzfulvene (*picrate*, yellow needles, m. p.  $115-116^\circ$ , sintering at  $102^\circ$ ), but at the ordinary temperature, after a week, a mixture of this and *ω*-dimethyl-3:4

*hydroxyisopropylbenzfulvene*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{CMe}_2) \\ \text{C}(\text{CMe}_2\text{OH}) \end{smallmatrix} \rangle \text{CH}$ , m. p. 97–98°. Dimethylbenzfulvene is not reduced by aluminium amalgam and moist ether, but is smoothly converted into 3-*isopropylindene*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CPr}^i \\ \text{CH}_2 \end{smallmatrix} \rangle \text{CH}$ , faintly yellow oil, b. p. about 230° (decomp.) or 113°/15 mm., by sodium and boiling absolute alcohol.

Indene condenses less readily with aromatic ketones than with acetone. By prolonged boiling with acetophenone and alcoholic sodium ethoxide, it yields *ω*-phenyl-*ω*-methylbenzfulvene, yellow crystals, m. p. 68–69°, b. p. 178–179°/5 mm., and by similar treatment it condenses with benzophenone to give *ωω*-diphenylbenzfulvene (Grignard, A., 1911, i, 193). These two substances are reduced by aluminium amalgam and moist ether to 3-*α*-phenyl-*ethylindene*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{CHMePh}) \\ \text{CH}_2 \end{smallmatrix} \rangle \text{CH}$ , b. p. 161°/5 mm. and 196°/15 mm., and 3-*benzhydrylindene*, colourless crystals, m. p. 113–114°, respectively. The colours of the three preceding benzfulvenes conform to expectation; they are less intensely coloured than the corresponding fulvenes, and are more intensely coloured than the corresponding dibenzfulvenes (fluorene derivatives).

3-*isopropylindene* condenses smoothly with benzaldehyde and with anisaldehyde in the presence of 27% methyl-alcoholic potassium hydroxide to form, after about twenty-four hours at the ordinary temperature, 1-*benzylidene*-3-*isopropylindene*,



yellow needles, m. p. 105.5°, and the corresponding *methoxybenzylidene* compound, yellow crystals, m. p. 81°, respectively. According to Thiele and Bühner's theory of the oscillating linking (A., 1906, i, 571), the latter of these two compounds ought also to be formed by the condensation of 3-*p*-methoxybenzylindene and acetone, but the product proves to be 3-*p*-methoxybenzyl-*ωω*-

*dimethylbenzfulvene*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{CMe}_2) \\ \text{C}(\text{CH}_2\text{C}_6\text{H}_4\text{OMe}) \end{smallmatrix} \rangle \text{CH}$ , faintly coloured, felted needles, m. p. 83°. This, like other aliphatic fulvenes, is not reduced by aluminium amalgam and moist ether, but is converted by sodium and boiling absolute alcohol into *p*-methoxybenzylisopropylindene, pale yellow oil, b. p. 200°/6 mm., which is also obtained by reducing 1-methoxybenzylidene-3-*isopropylindene* with aluminium amalgam and moist ether. The condensation of benzaldehyde with 3-*p*-methoxybenzylindene and anisaldehyde with 3-benzylindene (Thiele and Bühner, *loc. cit.*) as therefore been re-examined, and it is now found that the two reactions do not give rise to the same substance under suitable conditions. When the condensations are effected by the prolonged action of methyl-alcoholic potassium hydroxide at the ordinary temperature, the same product, 3-benzyl-1-*p*-methoxybenzylidene-

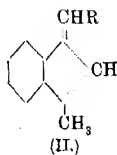
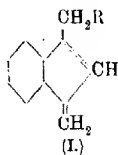
indene and *p*-chlorobenzaldehyde yield 3-benzyl-1-*p*-chlorobenzylideneindene, yellow needles, m. p. 88—89°. The last compound is converted by boiling for eight hours with methyl-alcoholic potassium hydroxide partly into a mixture, m. p. 79—81°, of the two isomerides and partly into 3-benzyl-1-*p*-chlorobenzylidene, colourless needles, m. p. 183—184°, which is also produced by reducing the benzfulvene with aluminium amalgam and moist ether.

3-*p*-Methylbenzylidene and *p*-chlorobenzaldehyde yield 3-*p*-methylbenzyl-1-*p*-chlorobenzylideneindene, large yellow crystals, m. p. 95—96°, together with a small quantity of a substance, colourless needles, m. p. 181—183°, which is probably 1-*p*-chlorobenzyl-3-*p*-methylbenzylidene. 3-*p*-Chlorobenzylidene and *p*-tolualdehyde yield a mixture of a colourless substance, m. p. 182—184° (which is shown to be 1-*p*-chlorobenzyl-3-*p*-methylbenzylidene), and a small quantity of a yellow substance, m. p. 91—92°, which appears to be 3-*p*-methylbenzyl-1-*p*-chlorobenzylideneindene in a not quite pure state.

C. S.

**Isomerism of Benzfulvenes and Indenes.** H. M. Wüster (*Annalen*, 1918, 415, 291—337. Compare two preceding abstracts).—With regard to the eight pairs of isomerides described by Thiele and Merck and by Berntsen (*loc. cit.*), no generalisation in respect of the stability of one of the two isomerides can be drawn, partly because no conclusions can be made from the nature of the groups introduced and partly because the transformation from the one isomeride into the other indubitably occurs only in two cases and fails entirely only in two other cases. A new series of benzfulvenes has therefore been examined.

The simplest case of isomerism is represented by a 3-substituted benzfulvene (formula I) and the isomeric  $\omega$ -substituted 3-methylbenzfulvene (formula II).



3-Methylbenzfulvene,  $C_6H_4 \langle \begin{smallmatrix} \text{CH} \\ \text{C}(\text{CH}_3) \end{smallmatrix} \rangle \text{CH}$ , an unstable faintly yellow, intensely odorous oil, b. p. 102—104°/11 mm (picrate, yellow needles, m. p. 125·5—126·5°), is readily obtained by boiling a mixture of 3-methylindene, paraformaldehyde, absolute alcohol, and 28% methyl-alcoholic potassium hydroxide for twelve minutes, but in no other case could a 3-substituted benzfulvene of type I be obtained, the product being always the  $\omega$ -substituted 3-methylbenzfulvene of type II, owing to the isomerising action of the alkali used as condensing agent.

Thus 3-benzylindene and paraformaldehyde yield 1-benzylidene-3-methylindene (*picrate*, pale red needles, m. p. 90–91°), 3-*p*-methoxybenzylindene and formaldehyde yield a mixture of 1-*p*-anisylidene-3-methylindene and 1-*p*-anisylidene-3-ethylindene,  $C_{18}H_{18}O$ , yellow needles, m. p. 100.5–101.5° (neither of these is changed by boiling for eight hours with methyl-alcoholic potassium hydroxide), 3-methylindene and furfuraldehyde yield, after condensation with methyl-alcoholic potassium hydroxide for forty-two hours at the ordinary temperature, 1-furfurylidene-3-methylindene, deep yellow needles, m. p. 77–77.5° (this compound, which forms a *picrate*, dark red needles, m. p. 97–98°, is also obtained by boiling 3-furylmethylindene, paraformaldehyde, absolute alcohol, and methyl-alcoholic potassium hydroxide for a few seconds and cooling rapidly), and 3-methylindene and benzophenone yield *ω*-*di*-phenyl-3-methylbenzfulvene, yellow crystals, m. p. 120–121° (*picrate*, pale red needles, m. p. 149–151°), the last condensation being effected by boiling with alcoholic potassium ethoxide for seventeen hours. The last-mentioned benzfulvene is also obtained by boiling a mixture of 3-benzhydrylindene, paraformaldehyde, absolute alcohol, and 28% methyl-alcoholic potassium hydroxide for one hour.

The preceding four benzfulvenes of type II are all intensely yellow, and are reducible by aluminium amalgam and moist ether; the reduction of *ω*-*di*-phenyl-3-methylbenzfulvene proceeds very slowly and incompletely, the product being 3-benzhydryl-1-methylindene,  $C_6H_5 \cdot \begin{smallmatrix} \text{C}(\text{CHPh})_2 \\ \text{CHMe} \end{smallmatrix} \text{CH}$ , colourless needles, m. p. 162.5–163.5°.

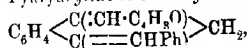
The groups phenyl, *p*-anisyl, benzhydryl, and furyl in all possible pairs have been systematically introduced into the *ω*- and *β*-positions in benzfulvene. The case of the pair phenyl and *p*-anisyl has been investigated by Thiele and Merck (*loc. cit.*); other isomerides are known, 3-benzyl-1-*p*-anisylideneindene being the more stable. Other pairs of isomerides which exhibit transposition are the following: 3-Benzhydrylindene and benzaldehyde are condensed by methyl-alcoholic potassium hydroxide, after one day at the ordinary temperature, or after thirty seconds in the boiling solution, yielding 3-benzhydryl-1-benzylideneindene, pale yellow needles, m. p. 131.5–132.5°. If the boiling is prolonged five minutes, a difficultly separable mixture of this and its isomeride, *ω*-*di*-phenyl-3-benzylbenzfulvene, deep yellow, quadratic crystals, m. p. 130–130.5°, is obtained. The transformation is easily and completely effected by boiling a mixture of 3-benzhydrylindene, benzaldehyde, pyridine, and 28% methyl-alcoholic potassium hydroxide for one minute. This method of preparing *ω*-*di*-phenyl-3-benzylbenzfulvene is much to be preferred to that in which 3-benzylindene and benzophenone are condensed by methyl-alcoholic potassium hydroxide, since in the latter considerable quantities of benzhydrol are formed. Thiele and Merck (*loc. cit.*) prepared 3-benzhydryl-1-*p*-anisylideneindene at the ordinary



temperature. It is also obtained at the b. p. after thirty seconds, but after boiling with alkali for one hour in alcoholic or pyridine solution, is transformed into *ω*-diphenyl-3-*p*-methoxybenzylbenzylfulvene, yellow needles, m. p. 127—128°. The preparation of the two following pairs of isomerides containing furyl and phenyl or *p*-anisyl groups at first presented great difficulty, on account of the extreme ease with which the unstable isomeride is converted into the stable one. 1-Furfurylideneindene (*ω*-furylbenzylfulvene),

$\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH} \\ \text{C}(\text{CH} \cdot \text{C}_6\text{H}_5\text{O}) \end{array} \right\rangle \text{CH}$ , yellow needles, m. p. 86—86.5° (*picrate*, red needles, m. p. 103—105°), prepared from indene and furfuraldehyde in boiling methyl-alcoholic potassium hydroxide (five minutes), is reduced by aluminium amalgam and moist ether to 3-furylmethylindene,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH}_2 \\ \text{C}(\text{CH}_2 \cdot \text{C}_6\text{H}_5\text{O}) \end{array} \right\rangle \text{CH}$ , almost colourless liquid with a pleasant, aromatic odour, b. p. 166—168°/15 mm.

From the last compound and benzaldehyde 3-furylmethyl-1-benzylideneindene, yellow needles, m. p. 93—94.5° (clear at 98°), must be obtained merely by shaking with hot methyl-alcoholic potassium hydroxide and immediately pouring the mixture into water. If the mixture is boiled even for only thirty seconds, the substance is transformed into 1-furfurylidene-3-benzylideneindane,

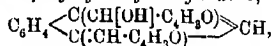


faintly yellow needles, m. p. 160.5—161°, which by boiling with methyl-alcoholic potassium hydroxide for four hours is converted into 1-furfurylidene-3-benzylidene, yellow needles, m. p. 126—127°; the last substance is obtained directly by the condensation of 3-benzylidene and furfuraldehyde. Using *p*-anisaldehyde in place of benzaldehyde, the following substances are obtained by methods similar to the preceding: 1-anisylidene-3-furylmethylindene, yellow leaflets, m. p. 88—89°. 1-anisylidene-3-furfurylideneindane, yellow needles, m. p. 150—150.5°, and 3-*p*-methoxybenzyl-1-furfurylideneindene, golden-yellow leaflets, m. p. 127—128°. The condensation of 3-benzhydrylidene and furfuraldehyde by methyl-alcoholic potassium hydroxide, whether boiled for three seconds or for one hour, yields 3-benzhydryl-1-furfurylideneindene, yellow needles, m. p. 170—170.5°, which is not changed by alkali even in the presence of pyridine. The isomeride was not prepared.

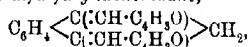
An examination of all the preceding pairs of isomerides shows that in every transformation the double linking shifts, so that the partial valencies are balanced as much as possible, and consequently the more saturated system is formed. In the four cases in which the substituents are a methyl group and an aromatic group, the more saturated system is formed so easily that the more unsaturated isomeride is unknown. When the substituents are two aromatic groups, a partial balance of the valencies occurs in both isomerides, and the transformation is rendered more difficult and leads to the formation of the isomeride in which the exocyclic

double linking is conjugated with the more strongly unsaturated substituent; this isomeride is therefore the more intensely coloured of the pair.

1-Furfurylidene-3-furylhydroxymethylindene,



yellow needles, m. p. 114·5—115°, obtained by condensing indene and furfuraldehyde by means of cold methyl-alcoholic potassium hydroxide for six hours, is reduced by aluminium amalgam and moist ether to 1:3-difurfurylideneindane,



faintly yellow needles, m. p. 132·5—133·5°, which is also obtained by boiling for one minute with alcoholic alkali 3-furylmethyl-1-furfurylideneindene, yellowish-brown needles, m. p. 103—104°, prepared from 3-furylmethylindene and furfuraldehyde.

3-Arylated benzfulvenes containing two aliphatic groups in the  $\omega$ -positions are quite generally incapable of transformation.  $\omega$ -Methyl- $\omega$ -ethylbenzfulvene, prepared by boiling indene and methyl ethyl ketone with alcoholic alkali for five hours, is a faintly yellow oil, b. p. 151—152°/15 mm. (*picrate*, orange needles, m. p. 37·5—88°, sintering at 85°), which is reduced by sodium and absolute alcohol to 3-isobutylindene, a colourless oil, b. p. 116—118°/12 mm. The last substance and benzophenone condense when boiled for twenty-three hours with pyridine and alcoholic alkali to form  $\omega\omega$ -diphenyl-3-isobutylbenzfulvene, yellow needles or stout prisms, m. p. 91—92°. 3-Benzhydryl- $\omega$ -methyl- $\omega$ -ethylbenzfulvene, prepared from 3-benzhydrylindene and methyl ethyl ketone and boiling alcoholic alkali (fifteen minutes), is a faintly yellow, crystalline powder, m. p. 149·5—151°. 3-isoPropylindene and benzophenone yield  $\omega\omega$ -diphenyl-3-isopropylbenzfulvene, yellow, crystalline powder, m. p. 127—128°. 3-Benzhydrylindene and acetone yield 3-benzhydryl- $\omega\omega$ -dimethylbenzfulvene, yellow, crystalline powder, m. p. 174—175°.

The reduction of 3-benzhydryl-1-benzylideneindene and of  $\omega\omega$ -diphenyl-3-benzylbenzfulvene by aluminium amalgam and moist ether leads to the same product, namely, a mixture of a substance,  $\text{C}_{20}\text{H}_{24}$ , hard crystals, m. p. 130—131°, and an isomeric substance, slender needles, m. p. 137—138°, which are the two benzylbenzhydrylindenes; also the reduction of  $\omega\omega$ -diphenyl-3-isobutylbenzfulvene yields a mixture of two isomerides, namely, benzhydrylisobutylindene I, colourless needles, m. p. 121—123°, and benzhydrylisobutylindene II, slender needles, m. p. 94—95·5°. The latter is obtained from the former by boiling with alcoholic alkali for thirty minutes, and also from 3-benzhydryl- $\omega$ -methyl- $\omega$ -ethylbenzfulvene by reduction with sodium and alcohol.

The reduction of benzfulvenes in ethereal solution with platinum-black and hydrogen leads to the formation of indanes. Thus 3-benzhydryl- $\omega\omega$ -dimethylbenzfulvene yields 3-benzhydryl-1-iso-propylindane, slender needles, m. p. 126·5—127·5°, and  $\omega\omega$ -di-

phenyl-3-isobutylbenzfulvene yields 1-benzhydryl-3-isobutylindane, colourless crystals, m. p. 104—106°. C. S.

**Action of Sulphur on Organic Compounds. I. Hydrocarbons.** LUDWIK SZPERL (*Chemik Polski*, 1917, 15, 10—18; from *Chem. Zentr.*, 1918, i, 908. Compare following abstracts).—A review of the literature of the subject. H. W.

**Action of Sulphur on Organic Compounds. II. Diphenylmethane and Fluorene. Dibenzyl.** LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski*, 1917, 15, 19—22; from *Chem. Zentr.*, 1918, i, 908—909. Compare preceding abstract).—Contrary to the statement of Kaufmann, the authors

find that diphenyldiphenylene-ethylene,  $\text{CPh}_2\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}$ , is the main product formed when a mixture of diphenylmethane and fluorene is heated with sulphur until hydrogen sulphide ceases to be evolved; the substance separates from acetone in needles containing acetone of crystallisation, which is lost on exposure to air. It then has m. p. 229—229.5°. Tetraphenylethane, tetraphenylethylene, tetraphenylene-ethane, and tetraphenylene-ethylene are simultaneously produced.

Tetraphenylthiophen,  $\text{C}_{26}\text{H}_{20}\text{S}$ , m. p. 183—184°, is the sole product of the action of sulphur on dibenzyl at 260°. H. W.

**Action of Sulphur on Organic Compounds. III. Benzyl Alcohol, Diphenylcarbinol.** LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski*, 1917, 15, 23—27; from *Chem. Zentr.*, 1918, i, 909. Compare preceding abstracts).—Visible reaction between benzyl alcohol and sulphur commences at about 180°, water, hydrogen sulphide, and benzaldehyde being evolved. The product of the reaction contains, in addition, benzoic acid, tetraphenylthiophen, stilbene, and small quantities of needles. m. p. 127—130°. The main products are tetraphenylthiophen and benzoic acid.

Diphenylcarbonyl ether,  $\text{C}_{20}\text{H}_{12}\text{O}$ , m. p. 108.5—109°, together with small quantities of benzophenone and possibly traces of diphenylmethane, is produced when diphenylcarbinol is heated with sulphur at 180°, and the action is stopped when water vapour ceases to be evolved. The formation of the ether is attributed to the catalytic action of sulphur on the alcohol. Similarly, benzyl alcohol when heated with 0.1 gram-atom of sulphur gives a 20% yield of dibenzyl ether, b. p. 295—298°. It is therefore to be assumed that the products isolated from the alcohols are due to the action of sulphur on the ethers, and not on the alcohols themselves. H. W.

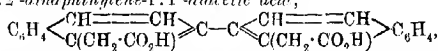
**Action of Sulphur on Organic Compounds. IV. Dibenzyl Ether and Benzhydryl Ether.** LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski*, 1917, 15, 28—33; from *Chem. Zentr.*, 1918, i, 909—910. Compare preceding abstracts).—With the object of verifying the hypothesis that the formation of the corresponding ethers from benzyl alcohol and diphenylcarbinol

is to be attributed to the catalytic action of sulphur, and that other possible admixtures are without influence, the following experiments have been performed. Pure benzyl alcohol was heated at  $180^\circ$  for several hours alone and with intermittent treatment with hydrogen sulphide; the results were negative. Slightly impure diphenylcarbinol (prepared from benzaldehyde and phenyl magnesium bromide and containing traces of magnesium, chlorine, etc.) gave after three hours at  $150$ – $152^\circ$  an almost quantitative yield of benzhydryl ether, but the change proceeded less rapidly with a purer material.

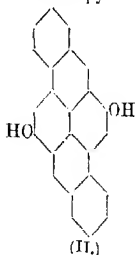
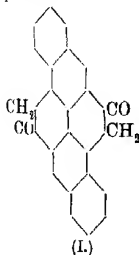
Benzyl ether, when heated with sulphur below  $200^\circ$ , yielded hydrogen sulphide, benzaldehyde, benzoic acid, stilbene, and tetraphenylthiophen. Diphenylcarbinyl ether gave benzophenone and tetraphenylethylene. The reactions occurred, therefore, in precisely the same manner as with the corresponding alcohols; they may be represented by the schemes:  $2(\text{PhCH}_2)_2\text{O} + 2\text{S} = 2\text{H}_2\text{S} + 2\text{C}_6\text{H}_5\cdot\text{CHO} + \text{CHPh}\cdot\text{CHPh}$ ,  $2(\text{Ph}_2\text{CH})_2\text{O} + 2\text{S} = 2\text{H}_2\text{S} + 2\text{COPh}_2 + \text{CPh}_2\cdot\text{CPh}_2$ . H. W.

**Attempted Synthesis of 3:4:8:9-Dibenzopyrene.** RICHARD WEITZENBÖCK (*Monatsh.*, 1918, **39**, 307–313).—By the synthetic method already discovered for pyrene (Weitzenböck, A., 1913, i. 259), it should be possible to produce pyrene derivatives containing condensed hydrocarbon nuclei; the paper records an unfinished investigation in this direction.

1:1'-Dimethyl-2:2'-dinaphthyl, prepared by the action of copper on 2-iodo-1-methylnaphthalene (Scholl, this vol. i. 484), is accompanied by a substance,  $\text{C}_{22}\text{H}_{16}$ , leaflets, m. p.  $314$ – $316^\circ$ ; *picrate*, brick-red needles, m. p.  $199$ – $201^\circ$ . When brominated in boiling nitrobenzene solution, 1:1'-dimethyl-2:2'-dinaphthyl is converted into 1:1'-dibromomethyl-2:2'-dinaphthyl,  $\text{C}_{22}\text{H}_{16}\text{Br}_2$ , needles, m. p.  $200$ – $201^\circ$ , which reacts with aqueous-alcoholic potassium cyanide, yielding 2:2'-dinaphthylene-1:1'-diacetonitrile, crystals, m. p.  $264^\circ$ ; this on hydrolysis with alcoholic potassium hydroxide at  $150^\circ$  gives 2:2'-dinaphthylene-1:1'-diacetic acid,



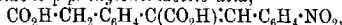
from this, by the stages represented by formulæ I and II, it should be possible to obtain 3:4:8:9-dibenzopyrene (formula III).



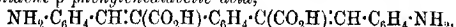
In a preliminary investigation with a view to a new pyrene synthesis, *o*-iodophenyldichloropropionic acid, obtained by the action of chlorine on a carbon disulphide solution of *o*-iodocinnamic acid, was steam distilled in the presence of excess of sodium carbonate, with formation of *o*-iodostyryl chloride,  $C_6H_4I \cdot CH:CHCl$ , b. p.  $151^\circ/24$  mm.

D. F. T.

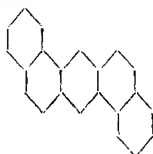
**Synthesis of the Isomeric Hydrocarbons 1:2:5:6-Dibenzanthracene and 3:4:5:6-Dibenzphenanthrene.** RICHARD WEITZENBÖCK and ALBERT KLINGLER (*Monatsh.*, 1918, **39**, 315—323. Compare Weitzenböck and Lieb, A., 1912, i, 547).—When heated with *o*-nitrobenzaldehyde in acetic anhydride solution, potassium phenylenediacetate undergoes conversion into *o*-nitrobenzylidene-*p*-phenylenedi-acetic acid,



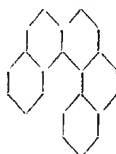
colourless needles, m. p.  $236^\circ$ , which by further treatment can be made to yield *di-o*-nitrobenzylidene-*p*-phenylenedi-acetic acid,  $NO_2 \cdot C_6H_4 \cdot CH : C(CO_2H) \cdot C_6H_4 \cdot C(CO_2H) : CH \cdot C_6H_4 \cdot NO_2$ , pale yellow prisms, m. p.  $308^\circ$  (decomp.). This substance on reduction in ammoniacal solution with ferrous hydroxide gives *di-o*-amino benzylidene-*p*-phenylenedi-acetic acid,



yellow needles, m. p. near  $276^\circ$ , which by diazotisation and subsequent treatment with copper powder can be made to yield a mixture of 1:2:5:6-dibenzanthracenedicarboxylic acid and 3:4:5:6-dibenzphenanthrenedicarboxylic acid; these were not separated, the mixture being directly converted by heating under reduced pressure into a mixture of the corresponding hydrocarbons, which were then separated by crystallisation from acetic acid. The less soluble 1:2:5:6-dibenzanthracene (formula I) forms silvery leaflets, m. p.  $262^\circ$  (picrate,  $C_{22}H_{14} \cdot 2C_6H_3O_2N_3$ , orange needles, m. p.  $214^\circ$ ), gives a red solution with alkaline sodium hyposulphite solution and is oxidisable by potassium dichromate in acetic acid to 1:2:5:6-dibenzanthraquinone,  $C_{22}H_{12}O_2$ , orange needles, m. p.  $248$ — $249^\circ$ , whilst the more soluble 3:4:5:6-dibenzphenanthrene (formula II) forms colourless needles, m. p.  $145$ — $146^\circ$ .



(I.)



(II.)

D. F. T.

**Preparation of Hydrogenated Compounds.** FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P., 305347; from *Chem. Zentr.*, 1918, i, 977).—The process depends on the action of alkali or alkali earth metals and alcohols on isocyclic or heterocyclic bases

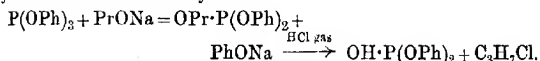
in the presence of an inert solvent; the alcohol is preferably added at the same rate as it is used in the reaction. Thus tetrahydro- $\alpha$ -naphthylamine is formed when a solution of  $\alpha$ -naphthylamine in alcohol is added to a mixture of solvent naphtha and sodium at a temperature above  $130^{\circ}$ ; with a solvent of lower b. p., such as toluene, dihydro- $\alpha$ -naphthylamine is obtained. 2-Methylquinoline, when hydrogenated at above  $130^{\circ}$ , yields tetrahydro-2-methylquinoline, which gives a characteristic blood-red coloration with ferric chloride and potassium ferriyanide. The picrate has m. p.  $153-154^{\circ}$ .  
H. W.

**Phenylpropionamidine.** ROLAND SCHOLL [with E. BERTSCH] (*Monatsh.*, 1918, **39**, 238-240).—Phenylpropionamidine,  $\text{NH}:\text{C}(\text{Et})\text{NHPH}$ ,

m. p.  $72-73^{\circ}$  (Michael and Wing, A., 1886, 148, give  $68^{\circ}$ ), is formed when propionitrile is heated with aniline hydrochloride in a sealed tube at  $170-180^{\circ}$  for twelve hours; *hydrochloride*, hygroscopic; *hydrogen oxalate*, m. p.  $141-142^{\circ}$ ; *picrate*, m. p.  $152-153^{\circ}$ .  
D. F. T.

#### Phenyl and Alkyl Phenyl Esters of Phosphorous Acid.

T. MIŁOBENDZKI and K. SZULGIN (*Chemik Polski*, 1917, **15**, 66-75; from *Chem. Zentr.*, 1918, i, 914-915. Compare this vol., i. 477, 478, 479).—The action of alcohols on triphenyl phosphite leads to replacement of the phenyl groups, but isomerisation occurs simultaneously with the formation of phosphinic esters:  $\text{P}(\text{OPh})_3 + 3\text{PrOH} = \text{PPrO}(\text{OPr})_2 + 3\text{PhOH}$ . Diphenyl esters may be obtained by the use of sodium alkylloxides:



Triphenyl phosphite, b. p.  $235^{\circ}/18$  mm., is obtained in 91% yield by the gradual addition of phosphorus trichloride to a mixture of phenol and pyridine. It does not react with cold alcohols. Methyl alcohol at  $225^{\circ}$  transforms it completely into dimethyl methylphosphinate, b. p.  $181^{\circ}/754$  mm. *Dipropyl propylphosphinate* (formed, together with small quantities of tripropyl phosphite, in a similar manner) is a colourless liquid, b. p.  $126^{\circ}/18$  mm.,  $D_4^{20}$  1.0327,  $D_4^{25}$  1.0324. *Tripropyl phosphite* (by action of sodium propoxide [4 parts] and triphenyl phosphite [1 part] in benzene solution) has b. p.  $103^{\circ}/24$  mm., whilst *tributyl phosphite* has b. p.  $120^{\circ}/10$  mm. The action of sodium propoxide (1 part) on triphenyl phosphite (1 part) leads to the formation of *propyl diphenyl phosphite*, b. p.  $203-204^{\circ}/24$  mm.,  $D_4^{19}$  1.1153,  $D_4^{20}$  1.1149. *Butyl diphenyl phosphite* has b. p.  $198^{\circ}/12$  mm.,  $D_4^{20}$  1.0918,  $D_4^{25}$  1.0917. Propyl diphenyl phosphite is obtained in better yield by the gradual addition of diphenylphosphorous chloride,  $\text{P}(\text{OPh})_2\text{Cl}$ , to a mixture of propyl alcohol and pyridine; it is slowly hydrolysed by water or alkalis.

*Diphenyl phosphite*, b. p.  $218-219^{\circ}/25$  mm., is prepared by

saturating ice-cold diphenyl propyl phosphite with hydrogen chloride (1 mol.). The alkaline solution of the substance gives with ferric chloride a precipitate of the composition  $(\text{PhO})(\text{FeO})\text{POH}$  [?]. H. W.

***o*-Nitrosophenol. III. Preparation of *o*-Nitrosophenol as a Lecture Experiment [Reagent for Copper].** OSKAR BAUDISCH (*Ber.*, 1918, 51, 1058—1059. Compare A., 1916, i, 33).—A solution containing *o*-nitrosophenol may be quickly prepared as follows: a crystal or two of *o*-nitrophenol is dissolved in a few drops of hot acetic acid, cooled, diluted a little, covered with light petroleum, and shaken with a trace of zinc dust. The aqueous layer becomes pink owing to the formation of the zinc salt of *o*-nitrosophenol, but the free reagent is chiefly contained in the supernatant, green layer. If this solution is shaken with a trace of a copper salt, the petroleum becomes colourless and the aqueous layer deep red. This test for copper is said to be more sensitive than the ferrocyanide reaction. J. C. W.

**Preparation of Picramic Acid.** GRETE EGERER (*J. Biol. Chem.*, 1918, 35, 565—566).—Finely powdered picric acid (20 grams) is dissolved in 300 c.c. of alcohol, and 125 c.c. of ammonia (0.880) are added. After cooling to 30°, hydrogen sulphide is passed in rapidly, so that the temperature rises to 50—55° in fifteen minutes. The flask is then cooled in ice, while the stream of hydrogen sulphide is maintained for forty-five minutes. Crystals of ammonium picramate are deposited, and are collected and decomposed by the addition of 60 c.c. of acetic acid (1 part of glacial acid to 4 parts of water). After vigorous stirring, the picramic acid is collected, washed with a little water, and recrystallised from boiling water. Yield, 75 to 80% of the theoretical. H. W. B.

**Preparation of Derivatives of *p*-Aminophenol.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 116920, 1917; A., 1901, i, 533).—*p*-Aminophenyl allyl ether (Spiegel & Sabbath) is poisonous, but its acyl derivatives are not poisonous in therapeutic doses, and possess narcotic, sedative, and anti-neuralgic properties. *p*-Acetylaminophenyl allyl ether forms lustrous leaflets, m. p. 94°, readily soluble in alcohol, ether, and acetone, and somewhat readily so in hot water. The *lactyl* derivative forms lustrous leaflets, m. p. 87°, readily soluble in alcohol, ether, and benzene, and somewhat readily so in hot water; the *isovaleryl* derivative forms small, lustrous needles, m. p. 95°, and the *α-bromoisovaleryl* derivative forms lustrous leaflets, m. p. 131°. A. S.

**Compounds of *p*-Phenetidine.** L. REUTTER (*Schweiz. Apoth. Zeit.*, 1917, 56, 692; from *Chem. Zentr.*, 1918, i, 825—826).—Di-*p*-phenethylthiocarbamide, lead carbonate, alcohol, and aqueous potassium cyanate reacting first in the cold and then at 45° yield the nitrile,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}(\text{CN})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , yellow crystals.

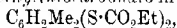
m. p.  $104^{\circ}$ , which is converted into a substance,  $C_{18}H_{21}O_2N_3S$ , yellow prisms, m. p.  $124^{\circ}$ , by shaking with yellow ammonium sulphide for three days, and finally warming at  $30-35^{\circ}$ , and into a substance,  $C_{18}H_{22}O_2N_3Cl$ , whitish-yellow crystals, m. p.  $220^{\circ}$ , by dissolution in concentrated hydrochloric acid on the water-bath.

C. S.

**Preparation of Guaiacol.** ERNST H. ZOLLINGER and HERMANN RÖHLING (D.R.-P., 305281; from *Chem. Zentr.*, 1918, i, 977).—A weak base such as sodium carbonate or sodium hydrogen carbonate is gradually added to a mixture of catechol with the alkali or alkali earth salts of methylsulphuric acid in the presence of veratrole as diluent at  $160-180^{\circ}$ ; the yield is more than 85% of that theoretically possible.

H. W.

**Polyhydric Mercaptans of the Benzene Series. VI. Homologous Dithiolbenzenes.** J. POLLAK and B. SCHADLER (*Monatsh.*, 1918, **39**, 129—148. Compare Pollak and others, *A.*, 1915, i, 529; 1914, i, 39; 1910, i, 734; 1909, i, 791).—By treatment with fuming sulphuric acid, *m*-xylene was converted into a mixture of disulphonic acids, from which by the action of phosphorus pentachloride a mixture of the corresponding *m*-xylene-2:4-disulphonyl chloride and *m*-xylene-2:5-disulphonyl chloride was obtained (compare Pfannenstill, *A.*, 1892, 1340). The crystalline 2:4-disulphonyl chloride on reduction with tin and hydrochloric acid gives 2:4-dithiol-*m*-xylene,  $C_6H_2Me_2(SH)_2$ , leaflets, m. p.  $123-125^{\circ}$  (acetyl derivative,  $C_6H_2Me_2(SAc)_2$ , leaflets, m. p.  $76.5-79^{\circ}$ ), which reacts with chloroacetic acid and ethyl chloroformate respectively in alkaline solution, yielding *m*-xylene-2:4-dithiolacetic acid,  $C_6H_2Me_2(S \cdot CH_2 \cdot CO_2H)_2$ , colourless, stellar aggregates, m. p.  $185-189^{\circ}$ , and 2:4-diethylthiocarbonato-*m*-xylene,



long needles, m. p.  $61-63^{\circ}$ , and is converted by aqueous hydrogen peroxide into a substance,  $(C_6H_2Me_2S_2)_n$ , needles, m. p.  $252-255^{\circ}$ ; with picryl chloride, the mercaptan reacts, producing 2:4-dipicrylthiol-*m*-xylene,  $C_6H_2Me_2[S \cdot C_6H_2(NO_2)_3]_2$ , orange-coloured needles with  $1C_6H_5$ , m. p.  $258-259.5^{\circ}$ . Treatment with methyl sulphate in the presence of alkali converts the mercaptan into 2:4-dimethylthiol-*m*-xylene,  $C_6H_2Me_2(SMe)_2$ , needles, m. p.  $83-84.5^{\circ}$ , which reacts with chlorine, yielding a substance,  $C_{10}H_{11}S_2Cl_3$ , and with bromine in chloroform solution, giving an additive compound,  $C_6H_2Me_2(SMe)_2Br_2$ , deep red needles, decomp.  $99-102^{\circ}$ ; this regenerates the parent dimethylthiolxylene when shaken in chloroform solution with aqueous sodium hydrogen sulphite. Oxidation with aqueous potassium permanganate converts the dimethylthiolxylene into the disulphone,  $C_6H_2Me_2(SO_2Me)_2$ , needles, m. p.  $187-188^{\circ}$ .

In a similar manner, the isomeric, oily *m*-xylene-2:5-disulphonyl chloride can be reduced to an oily 2:5-dithiol-*m*-xylene, b. p.  $142-144^{\circ}/9$  mm., which reacts with chloroacetic acid in alkaline



solution, giving *m*-xylene-2:5-dithiolacetic acid, stellar aggregates, m. p. 158—161°, and with picryl chloride forming 2:5-dipicrylthiol-*m*-xylene, crystals, m. p. 211—213°. The 2:5-dimethylthiol-*m*-xylene, b. p. 167—169°/14 mm., obtained by methylation with methyl sulphate, undergoes substitution when treated in chloroform solution with bromine, yielding a bromo-derivative,



crystalline scales, m. p. 122—123°. The unexpected greater ease of bromination of this dimethylthiolxylene as compared with its 2:4-isomeride led to a doubt as to whether the relative structures of these substances are really as assumed above (compare Zincke and Krüger, A., 1913, i, 44), but an attempt to decide this matter by heating the 2:4-disulphonyl chloride with thionyl chloride in the hope of replacing the  $-\text{SO}_2\text{Cl}$  groups by chlorine atoms was unsuccessful, the product being a substance,  $\text{C}_8\text{H}_5\text{O}_3\text{Cl}$ , crystalline scales, m. p. 76—77°, possibly 2:4-dichloro-*m*-phthaloyl chloride. A somewhat similar reaction to this was observed between 1:3-dimethoxybenzene-4:6-disulphonyl chloride and thionyl chloride at 170°, the product being a substance,  $\text{C}_8\text{H}_5\text{O}_3\text{Cl}$ , needles, m. p. 95—98°, possibly of the structure  $\text{C}_8\text{H}_5\text{Cl}_2(\text{O}\cdot\text{CH}_2\text{Cl})_2$  (compare Meyer, A., 1916, i, 134).

2:6(?)-Dithiol-*p*-xylene, b. p. 145.5°/11.5 mm. (diacetyl derivative, needles, m. p. 79.5—82.5°; *p*-xylene-2:6-dithiolacetic acid derivative, needles, m. p. 170.5—174.5°; dipicryl derivative, yellow, crystalline solid, m. p. 251—255°; dimethyl derivative, needles, m. p. 92—94°), is obtainable from *p*-xylene through the disulphonyl chloride.

D. F. T.

### Polyhydric Mercaptans of the Benzene Series. VII. Substituted Thiolbenzenes.

J. POLLAK, LUZIE VON FIEDLER, and HEINRICH ROTH (*Monatsh.*, 1918, **39**, 179—200. Compare Pollak and Schädler, preceding abstract).—The effect of the introduction of a methyl group on the m. p. of the polyhydric mercaptans is rather irregular; thus 1:3-dithiolbenzene and 2:4-dithiol-*m*-xylene have m. p. 25° and 121° respectively (*loc. cit.*), whereas the substitution of a methyl group into the nucleus of trithiolbenzene causes a small depression of the m. p. Further compounds were therefore prepared with the view of investigating the influence of such substitution more widely, but no general regularities were observed either with the m.p.'s or b.p.'s.

1-Ethylbenzene-2:4-disulphonic acid (barium salt, crystalline with  $2\frac{1}{2}\text{H}_2\text{O}$ ), obtained by the action of fuming sulphuric acid on benzene, was converted into the corresponding acid chloride,  $\text{C}_6\text{H}_5\text{Et}(\text{SO}_2\text{Cl})_2$ , by the action of phosphorus pentachloride on its sodium salt at 140—150°; the corresponding 1-ethylbenzene-2:4-disulphonamide,  $\text{C}_6\text{H}_5\text{Et}(\text{SO}_2\cdot\text{NH}_2)_2$ , m. p. 186—190°, was obtained from the chloride by the action of warm aqueous ammonia. On reduction with tin and hydrochloric acid, the acid chloride is converted into 2:4-dithiol-1-ethylbenzene,  $\text{C}_6\text{H}_5\text{Et}(\text{SH})_2$ , an oil, b. p. 150—152°/18—20 mm., which reacts with alkaline methyl sulphate,

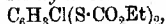
yielding 2:4-dimethylthiol-1-ethylbenzene,  $C_6H_3Et(SMe)_2$ , a pale yellow oil, b. p. 171—173°/14 mm., whilst with ethyl chloroformate and methyl chloroformate in the presence of alkali the products are colourless 2:4-diethylthiocarbonato-1-ethylbenzene,  $C_6H_3Et(S\cdot CO_2Et)_2$ , b. p. 224—226°/14 mm., and the corresponding 2:4-methyldithiocarbonato-1-ethyl benzene,  $C_6H_3Et(S\cdot CO_2Me)_2$ , a colourless oil, b. p. 217—220°/18 mm., respectively; the dithiol compound also reacts with chloroacetic acid in the presence of alkali and with picryl chloride, yielding, respectively, 1-ethylbenzene-2:4-dithiolacetic acid,  $C_6H_3Et(S\cdot CH_2\cdot CO_2H)_2$ , colourless crystals, m. p. 137—140°, and 2:4-dipicrylthiol-1-ethylbenzene,  $(C_6H_3Et[S\cdot C_6H_2(NO_2)_3])_2$ , yellow needles, m. p. 197·5—199°; when heated with sodium acetate and acetic anhydride, the dithiol compound is converted into the diacetyl derivative,  $C_6H_3Et(SAc)_2$ , b. p. 218—220°/18 mm., and in the presence of alcoholic ammonia is oxidised by concentrated hydrogen peroxide with formation of a substance,  $(C_6H_3EtS_2)_n$ . Nitric acid in the cold converts 2:4-dimethylthiol-1-ethylbenzene into 5-nitro-2:4-dimethylthiol-1-ethylbenzene,  $NO_2\cdot C_6H_2Et(SMe)_2$ , yellow, silky needles, m. p. 117—118°, whereas fuming nitric acid effects an oxidation to a monosulphoxide of the last product,  $NO_2\cdot C_6H_2Et(SMe)\cdot SMeO$ , yellow, silky needles, m. p. 119·5—120·5°.

In a similar manner to the preceding, 1-ethylbenzene-4-sulphonyl chloride was made to yield 4-thiol-1-ethylbenzene,  $C_6H_4Et\cdot SH$ , b. p. 91—93°/12—13 mm. (acetyl derivative,  $C_6H_4Et\cdot SAc$ , b. p. 136·5—140°/13—14 mm.), which in alkaline solution reacts with chloroacetic acid, giving 1-ethylbenzene-4-thiolacetic acid,  $C_6H_4Et\cdot S\cdot CH_2\cdot CO_2H$ , colourless, silky needles, m. p. 61—67°, and in alcoholic solution with picryl chloride, forming 4-picrylthiol-1-ethylbenzene,  $C_6H_4Et\cdot S\cdot C_6H_2(NO_2)_3$ , deep yellow, silky needles, m. p. 113·5—116°.

By treating phenol with fuming sulphuric acid, a mixture of sulphonic acids can be obtained which, on conversion into the corresponding sodium or potassium salts and heating with phosphorus pentachloride at 140—150°, yields a more soluble (in ether) 4-chlorobenzene-1:3-disulphonyl chloride,  $C_6H_3Cl(SO_2Cl)_2$ , needles, m. p. 87—88°, and a less soluble 2-chlorobenzene-1:3:5-trisulphonyl chloride,  $C_6H_2Cl(SO_2Cl)_3$ , pale yellow needles, m. p. 170—171°. The former product on reduction with tin and hydrochloric acid gives 4-chloro-1:3-dithiolbenzene,  $C_6H_3Cl(SH)_2$ , a pale yellow liquid, b. p. 145—146°/13—14 mm. (acetyl derivative,  $C_6H_3Cl(SAc)_2$ , b. p. 214—217°/19 mm.; picryl derivative,  $C_6H_3Cl[S\cdot C_6H_2(NO_2)_3]_2$ , golden-yellow platelets, m. p. 201—204°; dimethyl derivative,  $C_6H_3Cl(SMe)_2$ , pale yellow oil, b. p. 177—179°/18 mm.; 4-chlorobenzene-1:3-dithiolacetic acid,

$C_6H_3Cl(S\cdot CH_2\cdot CO_2H)_2$ , silky needles, m. p. 159—160°; the reaction with ethyl chloroformate followed an unusual course, the product under normal conditions consisting of 4-chloro-3(?)thiol-1(?)ethylthiocarbonato-benzene,  $SH\cdot C_6H_3Cl\cdot S\cdot CO_2Et$ , b. p. 204°/18 mm., the completely

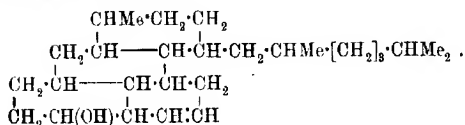
substituted 4-chloro-1:3-diethylthiocarbonatobenzene,



needles, m. p. 48—49°, being obtained only with the use of an excess of ethyl chlorocarbonate. The reduction of 2-chlorobenzene-1:3:5-trisulphonyl chloride gave 2-chloro-1:3:5-trithiolbenzene,  $\text{C}_6\text{H}_3\text{Cl}(\text{SH})_3$ , yellow crystals, m. p. 64—67°; methyl derivative,  $\text{C}_6\text{H}_3\text{Cl}(\text{SMe})_3$ , needles, m. p. 92—94°; 2-chlorobenzene-1:3:5-trithiolacetic acid,  $\text{C}_6\text{H}_3\text{Cl}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_3$ , colourless needles, m. p. 199—200°.

D. F. T.

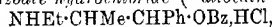
**Energetic Oxidation of Cholesterol by Nitric Acid.** ADOLF WINDAUS (*Zeitsch. physiol. Chem.*, 1918, **102**, 160—165).—The following compounds have been recognised among the products of the oxidation of cholesterol by nitric acid: dinitroisopropane and acetic, succinic, methylsuccinic, and  $\alpha$ -methylglutaric acids. Acetone, hydroxyisobutyric acid, methyl isohexyl ketone, and octane have previously been obtained, and the author points out that all these substances may be regarded as derived from an isooctyl side-chain in cholesterol. On this assumption, cholesterol may be represented by the formula



H. W. B.

**[Preparation of  $\beta$ -Diethylamino- $\alpha$ -phenylpropyl Benzoate and  $\beta$ -Ethylamino- $\alpha$ -phenylpropyl Benzoate.]** NAGAYOSHI

NAGAI (Brit. Pat. 117486, 1917).—The preparation of two new bases possessing local anæsthetic properties from  $\beta$ -amino- $\alpha$ -phenylpropanol ("mydriatin," Jap. Pat. 27056) is described. Mydriatin is converted into a mixture of its mono- and di-ethyl derivatives by treatment with an ethyl haloid, and the ethyl derivatives are dissolved in ether and benzoylated. The ethereal solution of the benzoyl compounds is shaken with dilute hydrochloric acid, and the aqueous and ethereal layers are separated. From the aqueous layer by evaporation under diminished pressure,  $\beta$ -diethylamino- $\alpha$ -phenylpropyl benzoate ("allocain S"),  $\text{NEt}_2\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{OBz}$ , is obtained as hydrochloride in the form of a colourless, transparent, vitreous mass. The ethereal solution contains *N*-benzylethylmydriatin. It is evaporated, the residue heated with 30% hydrochloric acid, diluted, filtered, shaken with ether, and the separated aqueous layer filtered and evaporated, whereon  $\beta$ -ethylamino- $\alpha$ -phenylpropyl benzoate hydrochloride ("allocain A"),



separates in flat needles. It is stated that benzoic esters of mono- and di-alkyl or mono- and di-aryl derivatives of mydriatin, and benzoic esters of aminophenyl alcohols homologous to mydriatin.

and of their alkyl or aryl derivatives, all possess more or less and of their alkyl or aryl derivatives, all possess more or less anæsthetic properties.

A. S.

### Coloured Acid Additive Products of Unsaturated Ketones.

FRITZ STRAUS [with HUGO BLANKENHORN] (*Annalen*, 1918, **415**, 232—256).—Mylo has shown (A., 1912, i, 4) that the acetals of aldehydes react with phosphorus pentachloride, thionyl chloride, etc., an alkyloxy-group being replaced by a chlorine atom. It is now shown that the acetals of certain unsaturated ketones in benzene solution react with hydrogen chloride or, better, phosphorus pentachloride (1 mol.) in the same way; the products are isolated in the form of the yellow or orange-red complex compound with phosphorus pentachloride or mercuric chloride. Thus the acetal of phenyl cinnamylidene methyl ketone in benzene solution is treated with phosphorus pentachloride (1 mol.) dissolved in the same solvent, and to the cooled, clear, faintly coloured solution is added drop by drop, with complete exclusion of moisture, a solution of mercuric chloride in dry ether, whereby the additive compound,  $\text{CHPh:CH:CH:CH}\cdot\text{CPhCl}\cdot\text{OMe}, \text{HgCl}_2$ , m. p. about  $110^\circ$  (decomp.), is precipitated as a red oil, which rapidly solidifies and becomes crystalline. In a similar way, the acetal of phenyl styryl ketone,  $\text{CHPh:CH}\cdot\text{CPh(OMe)}_2$ , colourless needles, m. p.  $46\text{--}46.5^\circ$ , yields the substance,  $\text{CHPh:CH}\cdot\text{CPhCl}\cdot\text{OMe}, \text{HgCl}_2$ , yellow crystals, m. p. about  $100^\circ$  (decomp.), the acetal of *pp'*-dimethoxybenzophenone, colourless needles, m. p.  $107\text{--}108^\circ$ ; yields the substance,  $\text{OMe}\cdot\text{CCl(C}_6\text{H}_4\cdot\text{OMe)}_2\cdot\text{HgCl}_2$ , yellow, apparently amorphous powder, and the acetal of benzophenone yields the substance,  $2\text{CPhCl}\cdot\text{OMe}, 5\text{HgCl}_2$ , almost colourless needles. These substances are converted into the original ketones by hydroxylic solvents, into the original acetals by alcoholic sodium methoxide, and evolve methyl chloride when heated.

The bearing of the preceding substances on the constitution of the coloured acid additive compounds of the ketones is discussed.

The following substances are described: *p*-chlorophenyl *p*-methoxystyryl ketone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH:CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl}$ , yellow needles, m. p.  $121\text{--}122^\circ$ , prepared from anisaldehyde and *p*-chloroacetophenone in aqueous alcohol containing about 0.5% of sodium hydroxide; *p*-anisyl *p*-chlorostyryl ketone, pale yellow crystals, m. p.  $130\text{--}131^\circ$ ; *p*-anisyl *p*-chlorocinnamylidenemethyl ketone, yellow needles, m. p.  $140^\circ$ ; *p*-chlorophenyl *p*-methoxycinnamylidenemethyl ketone, golden-yellow needles, m. p.  $156^\circ$ ; and *p*-chlorodistyryl ketone, pale yellow needles, m. p.  $134^\circ$ .

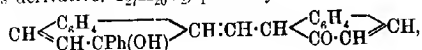
C. S.

**The Quinonoid Oxidation Product of Methylene-di-3-naphthol.** MORITZ KOHN and ALFONS ÖSTERSETZER (*Monatsh.*, 1918, **39**, 299—306).—The yellow quinonoid oxidation product of methylenedi- $\beta$ -naphthol was regarded by Abel (A., 1893, i, 172)

as having the peroxide structure,  $\text{C}_{10}\text{H}_6\langle\begin{smallmatrix} \text{CH}_2 \\ \text{O}_2 \end{smallmatrix}\rangle\text{C}_{10}\text{H}_6$ , but the

quinonoid formula,  $\text{CH}\langle\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH}\cdot\text{CO} \end{smallmatrix}\rangle\text{C:CH}\cdot\text{CH}\langle\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{CH} \end{smallmatrix}\rangle\text{CH}$ , is

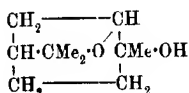
now proposed. This structure is in accordance with the formation of a *phenylhydrazone*,  $C_{27}H_{20}ON_2$ , orange-red needles, m. p. 153—156°, only the orthoquinonoid carbonyl group reacting with the usual reagents for ketonic substances; the phenylhydrazone on reduction with zinc and alcoholic acetic acid yields a *dihydro*-derivative,  $C_{27}H_{22}ON_2$ , a colourless powder, m. p. 133—136°; this derivative is probably a hydrazo-compound, whilst the parent phenylhydrazone is of azo-structure. With magnesium methyl iodide, the quinonoid compound reacts, forming a substance,  $C_{22}H_{18}O_2$ , probably  $CH \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \cdot \text{CMe}(\text{OH}) \end{smallmatrix} \text{C} : \text{CH} \cdot \text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \cdot \text{CH} \end{smallmatrix} \text{CH}$  needles, m. p. 135—145°, and with magnesium phenyl bromide an analogous derivative,  $C_{27}H_{20}O_2$ , probably



prisms, m. p. 130—170°, is obtained. Methyl sulphate converts methylenedi- $\beta$ -naphthol into the *dimethyl* ether,  $C_{25}H_{20}O_2$ , leaflets, m. p. 144—147°. D. F. T.

*cis-trans*.-Isomerism in the Terpene Series. Addition of **Hypochlorous Acid to Terpeneol**. K. SLAWINSKI (*Chemik Polski*, 1917, 15, 97—105; from *Chem. Zentr.*, 1918, i, 920—921).

—Terpeneol dissolved in acetic acid was treated with sodium hypochlorite solution (1%); the product could be separated by fractional crystallisation into two portions: (1) m. p. 114—115°, b. p. 162—165°/15 mm., and (2) m. p. 60—80°, b. p. 125—155°, both of which consisted of the chlorohydrin of menthane-1:2:8-triol. The crude substance was treated with potassium hydroxide (20%) and the product separated into a liquid and a solid portion (m. p. 118—118.5°). The former, on distillation, yielded small quantities of pinol and pinol hydrate (annexed formula), which could only



be derived from the *cis*-chlorohydrin of menthane-1:2:8-triol. From the fraction, b. p. 175—180°/13 mm, it was found possible to isolate *cis*-menthane-1:2:8-triol, m. p. 118—118.5°. The chlorohydrin of menthanetriol of m. p. 114—115° yielded almost exclusively pinol hydrate when treated with potassium hydroxide (20%), so that the chlorine atom must be attached to the carbon atom in position 6. From the mixture of chlorohydrins, m. p. 60—80°, only small amounts of the menthanetriol, m. p. 116—117.5°, could be isolated. The glycerol compound is therefore formed from the chlorohydrin of lower m. p. H. W.

**Constituents of Resins. II. Constituents of Sumatra Gum Benzoin.** HANS LIEB and ALOIS ZINKE (*Monatsh.*, 1918, 39, 219—230). —Unlike Siamese gum benzoin, Sumatra gum benzoin dissolves completely in hot dilute aqueous sodium hydroxide; the resulting solution, on boiling, deposits the sodium salt of 1-benzoresinol.

n. p. 339—341°,  $[\alpha]_D^{20}$  -12.88°, probably of the composition  $C_{14}H_{11}O_4$ . The mother liquors on the addition of a little ether deposit the sodium salt (needles with  $4H_2O$ ) of *d*-sumaresinol,  $C_{14}H_{15}O_4 \cdot H_2O$ , m. p. 298—299°,  $[\alpha]_D^{20} +51.60^\circ$  (methyl ether, crystals, m. p. 215—216°; ethyl ether, needles, m. p. 207—208°), isomeric with siaresinol (this vol., i, 398). The benzoiresinol of Joly (A., 1893, i, 480, 666) was probably a mixture of *d*-sumaresinol with *l*-benzoiresinol.

D. F. T.

### Vulcanisation without Sulphur by Ostromyslenski's Method. E. BUNSCHOTEN (*Kolloid Zeitsch.*, 1918, 23, [i], 25—31).

Nitrobenzene and *m*-dinitrobenzene alone have little vulcanising action on rubber, and such organic accelerators as *p*-nitrosodimethylaniline have no effect. Metallic oxides, however, act as strong catalysts, particularly lead oxide, which was used for all the experiments recorded. The rate of vulcanisation by *m*-dinitrobenzene depends on the sample of rubber used, and is increased by increasing the amount of catalyst or by increasing the temperature within the limits studied, 137—157°. The optimum time of heating varies as the other factors are varied, but if it is exceeded, the physical properties of the product deteriorate. Samples of rubber vulcanised with dinitrobenzene rapidly deteriorate, and white crystals of unchanged dinitrobenzene make their appearance on the surface.

The viscosity of benzene solutions of rubber is increased by addition of dinitrobenzene in the dark, particularly at high temperatures, but in the light the viscosity rapidly falls off. The opinion is expressed that the vulcanising action of such substances as dinitrobenzene is due to acceleration of polymerisation of the rubber. Sulphur acts in the same manner, but at the same time enters into combination with the rubber.

When rubber is heated with such inorganic oxidising agents as potassium permanganate, persulphate, dichromate, chlorate, nitrate, ceric acid, bleaching powder, or manganese dioxide, incipient decomposition sets in, but the product is still soluble in benzene after long standing. [See also *J. Soc. Chem. Ind.*, 665A.]

E. H. R.

**Scoparin.** J. HERZIG and GERTRUD TIRING (*Monatsh.*, 1918, 39, 33—267).—Goldschmiedt and von Hemmelmayr (A., 1893, 601; 1894, i, 542) have shown that scoparin, obtained from *partium scoparium*, contains a methoxyl group and six hydroxyl radicals, and attributed to the substance the formula  $C_{20}H_{20}O_{10}$ ; it was found possible to alkylate only one hydroxyl radicle. By using diazomethane, however, it is possible to obtain a dimethyl derivative (*trimethylnorscoparin*),  $C_{24}H_{28}O_{12}$ , yellow crystals, m. p. 50—265° (decomp.), and a trimethyl derivative (*tetramethylnorscoparin*),  $C_{28}H_{32}O_{14}$ , yellow crystals, m. p. 220—238°, together with an amorphous substance. With methyl iodide and silver

oxide, it is possible to convert scoparin into a crystalline *octa-methylnorscoparin*,  $C_{21}H_{12}O_3(OMe)_8$ , m. p. 120—130°, with subsequent resolidification and m. p. 229—233°. The composition of these substances, as also that of acetylscoparin, renders it probable that the molecular formula of scoparin is not  $C_{20}H_{20}O_{10}$ , but  $C_{22}H_{22}O_{11}$  (compare also Stenhouse, *Annalen*, 1851, **78**, 15.)

D. F. T.

**Synthesis of Alcohols in the Thiophen Series.** V. THOMAS and V. COUDERC (*Bull. Soc. chim.*, 1918, [iv], **23**, 326—328).—Magnesium thienyl iodide reacts with ketones, giving thiophenic alcohols, of which the following have been prepared.

*Diphenylthienylcarbinol*,  $HO \cdot CPh_2 \cdot C_4H_2S$ , which apparently condenses with aniline hydrochloride, giving a compound, colourless leaflets.

*Phenyldithienylcarbinol*,  $HO \cdot CPh(C_4H_2S)_2$ , m. p. 90°. With benzil, a compound [thienylphenylbenzoil?],  $C_4H_3S \cdot CPh(OH) \cdot COPh$ .

m. p. 56°, was obtained.

W. G.

**Eserine (Physostigmine).** J. HERZIG and HANS LIEB (*Monatsh.* 1918, **39**, 285—292).—The ordinary method for the determination of imino-methyl in eserine gives a result indicating the presence of two such groups, whereas the compound obtained after the removal of two methyl radicles, when examined by the micro-method, shows the presence of a third methyl group (Herzig and Meyer, this vol. i, 383; Straus, A., 1914, i, 78; 1915, i, 448); eseroline, when examined by the micro-method, also gives results almost twice as high for imino-methyl as by the macro-method (Straus, A., 1915, i, 448). This difference appears to be due to the larger proportion of hydriodic acid used in the micro-method, and if in the macro-method only 0.1 gram of eserine is taken to 20 c.c. of hydriodic acid, the result agrees with the presence of three imino-methyl groups. The reason of this peculiarity of eserine is at present undecided, although the possibility that the third and residual radicle is an ethyl group, and not a methyl, receives some support from the behaviour of eserine when examined by Kirmal as Bühn's method for methyl determination (A., 1914, ii, 497; 1914, ii, 154).

D. F. T.

**The Alkaloids of the Calabar Bean. VII. Degradation by successive Iodomethylations of the Nuclei of Eserine and Geneserine.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1918, [iv], **23**, 335—356. Compare A., 1915, i, 891, 892).—Eserethole methiodide (*loc. cit.*), when decomposed in aqueous solution with sodium carbonate, yields *eseretholemethine*, previous m. p. 80°.  $[\alpha]_D + 10^\circ$ , which gives a *hydriodide*, m. p. 170°. *hydrochloride*, and a *zincchloride*, m. p. 193°. It is a tertiary base and gives a quaternary *methiodide*, m. p. 100°.  $[\alpha]_D - 11.8^\circ$  which when decomposed with aqueous potassium hydroxide yields

rimethylamine and a new base, *etheserolene*,  $C_{12}H_{12}N \cdot OEt$ , an oil, giving an oily bromo-derivative and a crystalline nitro-derivative.

With methyl iodide, geneserine gives three compounds, one of which, m. p.  $215^{\circ}$  (*loc. cit.*), previously described as a methiodide, is really  $\psi$ -geneserinemethine hydriodide, from which the free base is obtained as an uncrystallisable syrup, giving a methiodide, m. p.  $169^{\circ}$  (decomp.),  $[\alpha]_D -15^{\circ}$ . This methiodide is also one of the products of iodomethylation of geneserine, and when decomposed by alkalis yields methylamine and  $\psi$ -geneserolenemethine methiodide, m. p.  $261^{\circ}$ . The hydriodide, m. p.  $215^{\circ}$ , described above, when saponified by alkalis, yields  $\psi$ -geneserolenemethine, m. p.  $171^{\circ}$ ,  $[\alpha]_D -46^{\circ}$ , giving a hydriodide, m. p.  $234^{\circ}$ . With ethyl toluenesulphonate, it yields  $\psi$ -geneseretholemethine, and on acetylation gives acetylgeneserolenemethine, of which the methiodide has m. p.  $175^{\circ}$ . The methiodides of  $\psi$ -geneserinemethine or  $\psi$ -geneserolenemethine when treated with sodium hydroxide yield geneserolene,  $HO \cdot C_{12}H_{12}ON$ , m. p.  $215^{\circ}$ .

Eserine methiodide is converted by the action of hydrogen peroxide into  $\psi$ -geneserinemethine, and, similarly, eserethole yields geneseretholemethine, giving a hydriodide, m. p.  $212^{\circ}$ , and a ethiodide, m. p.  $130-140^{\circ}$ .

W. G.

#### The Alkaloids of the Calabar Bean. VIII. Hydrogenation in the Eserine, Geneserine, and $\psi$ -Geneserine Series.

LAX POLONOVSKI (*Bull. Soc. chim.*, 1918, [iv], 23, 356-361).—serine and a number of its derivatives, when reduced by zinc and hydrochloric acid, yield dihydro-derivatives, the following being described.

Neither dihydroeserine nor its salts crystallise readily, but a *hydrate*, m. p.  $100^{\circ}$ , was obtained.

Dihydroeseroline, m. p.  $140^{\circ}$ , gave a *picrate* and a *zincchloride*, m. p.  $194^{\circ}$ ,  $[\alpha]_D -95^{\circ}$ .

Dihydroeserethole, an oil, gave a *zincchloride*, m. p.  $252^{\circ}$ .

Dihydroeseretholemethine, an oil, gave a *zincchloride*, m. p.  $12^{\circ}$ , and a *methiodide*, m. p.  $127^{\circ}$ .

Geneserine and its derivatives on reduction gave, first, the corresponding eserine derivatives, and then their dihydro-derivatives.

Eserine methiodide when reduced by zinc and hydrochloric acid a alcoholic solution gave dihydroeserinemethine, m. p.  $125^{\circ}$ ,  $[\alpha]_D +11^{\circ}$ , which gave a *zincchloride*, m. p.  $160^{\circ}$ , and a *methiodide*. Seroline methiodide similarly gave dihydroserolinemethine, m. p.  $28-129^{\circ}$ .

W. G.

**Dihydrophenazine and Dihydroacridine.** ROLAND SCHOLL with W. NEUBERGER [*Monatsh.*, 1918, 39, 238].—Dihydrophenazine and dihydroacridine are formed when phenazine and acridine, respectively, in hot alcoholic solution are gradually introduced into an aqueous-alcoholic alkaline solution of sodium hypophosphite.

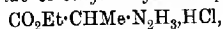
D. F. T.



**Tetramethyl-3:3'-diaminodiphenylmethane.** <sup>RUSSIAN</sup>  
 SCHOLL [with Jos. LENKO] (*Monatsh.*, 1918, **39**, 236—237).—When heated with methyl iodide and methyl alcohol at 140—150°, 3:3'-diaminodiphenylmethane is converted into the methiodide,  $C_{19}H_{25}N_2I_2$ , needles, m. p. 165°, of *tetramethyl-3:3'-diaminodiphenylmethane*,  $C_{17}H_{22}N_2$ , the oily, free base being obtainable by heating the methiodide with soda-lime in an atmosphere of hydrogen or with concentrated aqueous ammonia in a sealed tube at 180—190°. D. F. T.

**Hydrazino-acids. I.** AUGUST DARAPSKY (*J. pr. Chem.*, 1917, [ii], **96**, 251—327).—This communication opens with a general review of the subject and a theoretical discussion of the new results, which are grouped under three headings.

I. REDUCTION OF THE HYDRAZONE OF PYRUVIC ACID AND THE HYDRAZONE AND AZINE OF PHENYLGLYOXYLIC ACID, pp. 273—280 [with MORESHWAR PRABHAKAR].—The hydrazine salt of pyruvic acid hydrazone,  $NH_2 \cdot N : CMe \cdot CO_2H \cdot N_2H_4$  (Curtius and Lang, A., 1891, 452), is reduced by means of sodium amalgam, the product is evaporated to dryness with hydrochloric acid, and then esterified, when the *hydrochloride of ethyl  $\alpha$ -hydrazinopropionate*,



is obtained in white leaflets, m. p. 108—110° (decomp.). This is identified by conversion into the free acid and its benzylidene compound (Traube and Longinescu, A., 1896, i, 340; Thiele and Bailey, A., 1899, i, 169).

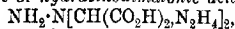
Phenylglyoxylic acid, which is conveniently prepared by oxidising mandelic acid with alkaline permanganate, reacts with alcoholic hydrazine hydrate to give the *hydrazine salt of phenylglyoxylic acid hydrazone*,  $NH_2 \cdot N : CPh \cdot CO_2H \cdot N_2H_4$ , which crystallises in long needles, m. p. 160—161°, and yields hydrazinophenylacetic acid on reduction with sodium amalgam (see below). The salt also changes into the azine of phenylglyoxylic acid,  $N_2(CPh \cdot CO_2H)_2$  (Bouveault, A., 1898, i, 585), when mixed with hydrochloric acid, and the same product may be obtained by warming phenylglyoxylic acid with hydrazine sulphate solution. The azine yields *hydrazinophenylacetic acid*,  $N_2H_3(CHPh \cdot CO_2H)_2$ , m. p. 160—161°, on reduction with sodium amalgam, and this gives an *ethyl ester*, slender needles, m. p. 88—89°.

II. ACTION OF HYDRAZINE HYDRATE ON BROMOACETIC,  $\alpha$ -BROMOPROPIONIC,  $\alpha$ -BROMOISOBUTERIC, BROMOMALONIC, AND BROMOPHENYLACETIC ACIDS, pp. 280—300 [with MORESHWAR PRABHAKAR].—The hydrochlorides of ethyl hydrazinoacetate (Traube and Hoffa, A., 1898, i, 235) and ethyl  $\alpha$ -hydrazinopropionate (above) may be prepared by boiling together alcoholic solutions of hydrazine hydrate and the corresponding bromo-acids, and then saturating the mixtures with hydrogen chloride.  *$\alpha$ -Hydrazinoisobutyric acid*,

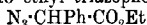


separates in sparingly soluble leaflets, m. p. 230—235° (decomp.)

when hydrazine hydrate and  $\alpha$ -bromoisovaleric acid are boiled together in alcohol; it forms a *benzylidene* compound, m. p.  $121^{\circ}$ , and a *diacetyl* derivative, m. p.  $205^{\circ}$ . Bromomalonic acid gives the *dihydrazine* salt of *hydrazinodimalonic acid*,



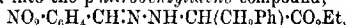
in long, pale yellow needles, m. p.  $209^{\circ}$  (decomp.). Bromophenylacetic acid (from mandelic acid and hydrobromic acid) yields *hydrazinophenylacetic acid*,  $\text{N}_2\text{H}_5\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  (above), in white leaflets, m. p.  $189$ – $190^{\circ}$  (decomp.). This forms a *benzylidene* compound, m. p.  $150^{\circ}$ , a *salicylidene* compound, m. p.  $153$ – $154^{\circ}$ , and a *dibenzoyl* derivative, m. p.  $169$ · $5$ – $170^{\circ}$ . It is oxidised by ferric chloride to benzaldazine and hydrazine chloride, and is converted into chloro- and bromo-phenylacetic acids by means of the halogens, and into mandelic acid by means of nitrous acid. The *ethyl* ester is an insoluble, yellow oil, which forms a *hydrochloride*, n. p.  $138^{\circ}$  (decomp.), a *hydrobromide*, m. p.  $142$ · $5^{\circ}$ , and a *salicylidene* compound, slender, pale yellow needles, m. p.  $107^{\circ}$ , and reacts with chlorine to give ethyl chlorophenylacetate. The *methyl* ester also yields a *hydrochloride*, m. p.  $148$ – $148$ · $5^{\circ}$ . The salts of the esters react with potassium cyanate to give esters of *carbamyldiazinophenylacetic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{N}(\text{NH}_2)\cdot\text{CHPh}\cdot\text{CO}_2\text{R}$ . The *ethyl* ester has m. p.  $102$ · $5$ – $103^{\circ}$ , and forms a *hydrochloride*, m. p.  $153^{\circ}$ , and *salicylidene* compound, m. p.  $149$ · $5^{\circ}$ . The *methyl* ester has m. p.  $141^{\circ}$ . The hydrochloride of the *ethyl* ester also reacts with sodium nitrite to form *ethyl nitrosohydrazinophenylacetate*,  $\text{NH}_2\cdot\text{N}(\text{NO})\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ , in silky needles, m. p.  $59^{\circ}$ , which gives the violet coloration with ferric chloride typical of nitrosohydrazines. This ester reacts with a further quantity of nitrous acid to give ethyl phenyldiazoacetate and then ethyl mandelate, decomposes at  $110^{\circ}$  into nitrous oxide and ethyl phenylglycine, and changes into ethyl triazophenylacetate,



(Forster and Müller, T., 1910, 97, 138), when distilled with 10% sulphuric acid.

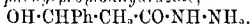
III. ACTION OF HYDRAZINE HYDRATE ON  $\alpha$ - AND  $\beta$ -BROMO- $\beta$ -BENZYLPROPIONIC ACID, pp. 301–327 [with HERBERT BERGER].—Bromo- $\beta$ -phenylpropionic acid is obtained as follows: ethyl enzylmalonate (Leuchs, A., 1911, i, 602) is hydrolysed by shaking with an excess of potassium hydroxide (5 mols.), the free acid then brominated in ethereal solution, and the bromobenzylmalonic acid is heated at  $125$ – $130^{\circ}$ . The acid is converted into hydrazino- $\beta$ -phenylpropionic acid,  $\text{NH}_2\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ , by means of alcoholic hydrazine hydrate, and the product agrees with Traube and Longinescu's description (*loc. cit.*). It forms a *hydrochloride*, benzylidene and salicylidene compounds (*ibid.*), a *diacetyl* derivative, transparent tablets, m. p.  $190$ – $191^{\circ}$ , a *benzoyl* derivative, rhombic needles, m. p.  $190$ – $192^{\circ}$ , and it reacts with sodium nitrite and dilute sulphuric acid to give *hydroxy- $\beta$ -phenylpropionic acid* (Fischer and Zemplén, A., 1910, 100). It also reacts with alcoholic hydrogen haloids to give the

*hydrochloride* (leaflets, m. p. 125°) and *hydrobromide* (snow-white leaflets, m. p. 123—125°) of the *ethyl ester*, this being a yellow oil, which changes when kept or heated (125°/14 mm.) into *ethyl β-phenylpropionate*. The *hydrobromide* yields *ethyl α-bromo-β-phenylpropionate*, b. p. 169°/14—15 mm., when treated with bromine in hydrobromic acid solution, whilst the *hydrochloride* may be converted into the *p-nitrobenzylidene* compound,

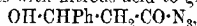


yellow rhombohedra, m. p. 87°, *ethyl α-semicarbazido-β-phenylpropionate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{Et}$ , needles, m. p. 147° (by means of potassium cyanate), and *ethyl α-nitrosohydrazino-β-phenylpropionate*,  $\text{NH}_2\cdot\text{N}(\text{NO})\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{Et}$ , pale yellow, silky needles, m. p. 61° (by means of a concentrated solution of sodium nitrite). The nitroso-ester is decomposed by heat (115—120°) into nitrous oxide and the *ethyl ester* of *phenylalanine*, whilst on warming with dilute sulphuric acid it yields the *ethyl ester* (b. p. 154°/14 mm.) of *α-azido-β-phenylpropionic acid*,  $\text{CH}_2\text{Ph}\cdot\text{CHN}_3\cdot\text{CO}_2\text{H}$ , this crystallising in large tablets, m. p. 24—27°, and forming an ammonium and a silver salt.

*β-Bromo-β-phenylpropionic acid* (from cinnamic acid and hydrogen bromide) reacts in quite another way with hydrazine hydrate. The product has the expected formula, but it is insoluble in alkalis and may be hydrolysed by hydrochloric acid. It is, in fact, *β-hydroxy-β-phenylpropionhydrazide*,



which crystallises in slender needles, m. p. 158°, and it is accompanied by some styrene and cinnamic acid. The hydrazide may also be prepared by the action of hydrazine hydrate on *ethyl β-hydroxy-β-phenylpropionate* (Findlay and Hickmans, T., 1909, 95, 1009). It forms a *benzylidene* compound, glistening leaflets, m. p. 179°, and reacts with nitrous acid to give the *azide*,



a pale yellow oil, which changes into *β-hydroxy-β-phenylpropionanilide*, m. p. 160°, when mixed with aniline.

It is mentioned that an alcoholic solution of hydrogen bromide can be obtained most readily by passing a current of dry hydrogen through warm bromine, then over platinised asbestos heated by a small flame, next through a tube containing red phosphorus, and finally into the alcohol.

J. C. W.

**The Methylation of Proteins.** J. HERZIG and KARL LAMPSTEINER (*Monatsh.*, 1918, 39, 269—284. Compare A., 1914, i, 753).—In the earlier investigation, it was shown that for various proteins the action of diazomethane gives products containing a fairly uniform percentage of methyl radicle, as indicated by the figures 3.68—4.86% of methoxyl group and 3.72—5.34% of methyl attached to nitrogen; silk fibroin alone was exceptional, the product from this containing 2.79% of methoxyl and 4.93% of iminomethyl, even after repeated methylation. Wool, after being submitted repeatedly to the action of diazomethane, contains 5.89%

of methoxyl and 6.28% of imino-methyl. In a similar examination of the alcohol-soluble proteins from grain, it was found that the zein of maize is rather resistant to diazomethane, giving after several treatments a product containing 4.17% of methoxyl and only 2.9% of imino-methyl; gliadin from wheat is more reactive, and gives a product containing 7.06% of methoxyl and 2.56% of imino-methyl. Non-coagulated serum-albumin from the horse gives results similar to those obtained with the coagulated product (*loc. cit.*).

[With F. ZIPPERER and M. QUITTNER.]—A similar examination was made of the effect on proteins of a ten-hour treatment with a boiling 1% solution of hydrogen chloride in methyl alcohol; the products gave the following analytical results: silk fibroin, 1.4% of methoxyl, imino-methyl proportion almost identical with that of the original substance; wool, 3.80% of methoxyl, 1.49% of imino-methyl. With zein, and particularly with gliadin, the hydrogen chloride causes considerable hydrolysis, a similar result being also obtained in the treatment of Witte's peptone. The product from zein contains 5.47—6.18% of methoxyl, but the imino-methyl content is almost unaltered. With gliadin, a large proportion passes into solution, the undissolved residue, as well as the portion of the dissolved material precipitable by ether, containing approximately 7% of methoxyl; it is probable that the extent of the hydrolytic effect of the methyl-alcoholic acid is greater than these figures indicate, because the resulting glutamic acid is remarkably resistant to esterification by this reagent. It is also probable that to some extent esterification products formed in the earlier stages of the treatment undergo subsequent hydrolysis by the action of water resulting from the interaction of the hydrogen chloride and methyl alcohol. The product of the reaction between zein or gliadin and methyl-alcoholic hydrogen chloride on treatment with diazomethane undergoes a marked increase in methoxyl content, which, however, is probably due in part to the presence of phenolic groups.

D. F. T.

**Legumin in Peas.** OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, 102, 85—104).—The legumin prepared from peas by extraction with salt solution and subsequent removal of the salt by dialysis (Osborne, A., 1896, i, 715) is soluble in dilute salt solutions, and thus differs from the insoluble legumin obtained from peas by extraction with water or dilute alkali, followed by precipitation with dilute acetic acid (Ritthausen, *J. pr. Chem.*, 1868, 103). The author proposes to designate the former as *a*-legumin and the latter as *b*-legumin. *b*-Legumin appears to be an acid meta-protein. *a*-Legumin also forms a compound with acid, which, however, is not *b*-legumin, because the latter swells in water, giving a viscid, non-filterable solution, whereas the acid compound of *a*-legumin does not swell in water, but gives a limpid, milky emulsion which filters readily, yielding an opalescent filtrate. Other slight differences in the properties of *a*- and *b*-legumins are

described, which indicate that *b*-legumin is not formed from *a*-legumin by the action of acid, alkali, or water, but is a distinct protein. H. W. B.

**Hæmoglobin, Bilirubin, and Urobilinogen.** W. C. de GRAAFF (*Chem. Weekblad*, 1918, 15, 1032—1045, 1059—1071).—A summary of the literature of the subject. A. J. W.

**Influence of Electrolytes on the Osmotic Pressure of Gelatin Solutions.** JACQUES LOEB (*J. Biol. Chem.*, 1918, 35, 497—508. Compare this vol., i, 413).—The osmotic pressures of solutions of gelatin which has been treated with acids, bases, and salts by the author's method (*loc. cit.*) are affected by the preliminary treatment which the gelatin has received in exactly the same way as the other properties so far examined, namely, swelling, viscosity, and resistance to precipitation by alcohol. The measurements were carried out by Lillie's method (*A.*, 1907, ii, 847), and the results demonstrate that gelatin treated with neutral salts and bases with univalent cation and acids with univalent anion has a greater osmotic pressure when dissolved in water than a solution of untreated gelatin, whilst salts and bases with bivalent cation and acids with bivalent anion do not produce any effect on the gelatin. H. W. B.

**Action of Chymosin and Pepsin. V. Action of the Enzymes on Legumin from Peas.** OLOF HANMARSTEN (*Zeitsch. physiol. Chem.*, 1918, 102, 105—147. Compare this vol., i, 470).—Chymosin acts on other proteins besides caseinogen, forming albumoses. Acid- and alkali-legumin are hydrolysed by chymosin in neutral solutions or in the presence of so little acid that no pepsin present would exert no, or but very little, hydrolytic action. The results are considered by the author to support the theory that assigns a separate identity to chymosin and pepsin. H. W. B.

**New Salts of 1:1-Dimethylarsepedine.** ENRIQUE V. ZAK and JUAN L. LANDABURU (*Bull. Soc. chim.*, 1918, [iv], 324—326. Compare *A.*, 1916, i, 575, 683).—The salts were prepared by neutralising a solution of 1:1-dimethylarsepedine hydroxide (*loc. cit.*, i, 575) in the presence of phenolphthalein with the requisite acid, the solution being evaporated to dryness over sulphuric acid and sodium hydroxide.

1:1-Dimethylarsepedine methochloride,  $\text{CH}_2\langle\text{CH}_2\text{CH}_2\rangle\text{AsMe}_2\text{Cl}$  has m. p. 237° (decomp.); the methobromide, an. p. 277—282 (decomp.).

1:1-Dimethylarsepedine sulphate has m. p. 232° (decomp.); the nitrate, m. p. 260° (decomp.); the hydrogen carbonate  $\text{C}_8\text{H}_{16}\text{AsHCO}_3$ , m. p. 156—157° (decomp.). W. G.

## Physiological Chemistry.

### The Haldane-Henderson Method for Estimating the Tension of Alveolar Carbon Dioxide and the Influence of Oxygen on the Stimulability of the Respiratory Centres.

MOTOI YAMADA (*Biochem. Zeitsch.*, 1918, 89, 27—47).—A new valve is described and figured for use with Henderson's modification of Haldane's method for estimating alveolar carbon dioxide. It was found that when the amount of carbon dioxide inhaled was greater than normal, the alveolar ventilation was better when the gas was mixed with pure oxygen than when mixed with air. Hence oxygen has a favourable influence on the breathing centre. No influence could be found to be exerted on the respiratory centre by the inhalation of pure oxygen.

S. B. S.

### The Influence of Atropine on Respiratory Metabolism and the Blood Gases.

GEORG KELEMAN (*Biochem. Zeitsch.*, 1918, 89, 338—349).—There is a marked diminution of the respiratory metabolism of dogs after intravenous injection of atropine, which effect can be antagonised by the simultaneous injection of pilocarpine. The increased gaseous metabolism produced by pilocarpine can be diminished by atropine, and the diminished gaseous metabolism produced by the latter alkaloid can be increased by the subsequent injection of the former. The content of the blood in carbon dioxide is diminished by injection of atropine. The diminished output of carbon dioxide produced by injection of atropine, already mentioned, is due, therefore, not to diminished secretion of this gas by the lungs, but to a general diminution of its production.

S. B. S.

### The Action of Pilocarpine on Respiratory Metabolism and the Gas Content of the Blood.

G. KELEMAN (*Biochem. Zeitsch.*, 1918, 89, 135—155).—The increased secretory activity of the salivary glands produced by pilocarpine is accompanied by an increased metabolism of energy (about 10%). There is also produced at the same time an increased carbon dioxide content in the blood, both venous and arterial. There is no evidence, however, of an increased "secretion" of carbon dioxide by the blood.

S. B. S.

### The Agglutination of Red Blood Corpuscles and the Hofmeister Series.

W. RADSMÅ (*Biochem. Zeitsch.*, 1918, 89, 1—219).—Blood corpuscles, suspended in a large amount of tonic solution of dextrose, readily agglutinate on addition of a small amount of a salt; 0.04% of sodium chloride is sufficient to bring out this phenomenon. The anions, in their activity as regards the agglutinative effect, follow the order of the Hofmeister series,

b b 2

and this indicates that some hydrophil colloid plays a part in maintaining the stability of a suspension of the corpuscles. S. B. S.

**The Action of Chlorates on the Blood of Man and certain Animals.** EGBERT CAESAR (*Biochem. Zeitsch.*, 1918, 89, 1—26).—Details are given as to the concentrations in which potassium chlorate exerts an injurious action on the blood, giving rise to the formation of methæmoglobin. The general conclusion is drawn that potassium chlorate can act toxically when taken *per os*, and that it should not be used indiscriminately in tooth-powders and analogous preparations. The astringent action of aluminium chlorate is due to the aluminium ion. A detailed criticism is given of a commercial preparation of chlorates known as Mallebrein's. S. B. S.

**Clinical Value of Freezing-point Determinations.** FRITZ EIGENBERGER (*Zeitsch. physiol. Chem.*, 1918, 102, 166—175).—The addition of urea, dextrose, or sodium chloride to a colloidal solution of gelatin, starch, or blood-serum produces scarcely any lowering of the freezing point, measured by Beckmann's method. When an acid or an alkali is added, a considerable depression may be observed, but it does not equal the calculated value. The author draws the conclusion that the determination of the freezing point of a pathological serum is not likely to furnish any valuable clinical information. H. W. B.

**The Influence of Oxygen on Metabolism. I. Experiments on Meal-worms.** TORBJÖRN GAARDER (*Biochem. Zeitsch.* 1918, 89, 48—93).—The metabolism of the *Tenebrio chrysalis* is independent of the oxygen tension of the atmosphere as long as the oxygen tension of the tissues is positive. As the oxygen tension of the atmosphere sinks, the gradient between the oxygen tension of the tissues and the atmosphere remains constant, until the former tension becomes zero. With further diminution of the tension of the oxygen of the atmosphere beyond this point, the gradient of oxygen tension between the tissue and atmosphere sinks, and the oxygen consumption of the chrysalis diminishes. Numerous numerical data are given in support of these statements, and the experiments were carried out by means of a modified micro-respirator of Krogh. If the chrysalis is allowed to remain in an atmosphere so poor in oxygen that the metabolism is sub-normal, certain anaerobic processes take place. On removing the animal to an atmosphere of normal oxygen content, the metabolism remains for some time sub-normal; it then increases and becomes greater than normal, and this is apparently due to the destruction of products formed during the anaerobic conditions. S. B. S.

**The Influence of Oxygen Tension on Metabolism. II. Experiments with Carp.** TORBJÖRN GAARDER (*Biochem. Zeitsch.* 1918, 89, 94—125).—An apparatus is figured and described for

passing water with known oxygen content through the gills of fish and estimating the consumption. It is found that there is a very slow increase in oxygen consumption with increasing tension of the oxygen dissolved in water. The increase is so small that the conclusion is drawn that the changes in oxygen tension in water which take place normally are without any appreciable effect in the metabolism. There is a linear relationship between oxygen consumption and the oxygen tension of the water passing the gills, that is, the oxygen consumption is in accordance with laws governing the absorption of gases by a liquid, and the increase of the consumption can be explained by assuming that the oxygen dissolved physically in the blood is utilised.

S. B. S.

#### Metabolism of Glycine given Intravenously at Constant

**Rates.** JULIAN H. LEWIS (*J. Biol. Chem.*, 1918, **35**, 567—576).—Glycine can be injected intravenously into a dog at the rate of 0.2 gram per kilo. of body weight per hour without causing the appearance of the amino-acid in the urine. The nitrogen is subsequently excreted at a slower rate in the form of urea.

H. W. B.

#### Significance of Glycollic Acid, Glyoxal, Glycollaldehyde, and Aminoacetaldehyde in Intermediary Metabolism.

ISIDOR GREENWALD (*J. Biol. Chem.*, 1918, **35**, 461—472).—The subcutaneous injection of glycollaldehyde and aminoacetaldehyde into phloridzinised dogs is followed in each case by an increased elimination of dextrose; similar injections of glyoxal or glycollic acid do not intensify the glycosuria. These results favour the view that glycine and dextrose are interchangeable in the organism in the following manner: glycine  $\rightleftharpoons$  aminoacetaldehyde  $\rightleftharpoons$  glycollaldehyde  $\rightleftharpoons$  dextrose.

H. W. B.

#### Nuclein Metabolism. V. Destruction of the Purine ring by Bacteria in the Human Intestine.

S. J. THANNHAUSER and G. DOREMÜLLER (*Zeitsch. physiol. Chem.*, 1918, **102**, 148—159. Compare this vol., i, 47).—After twenty days' incubation of deosine, guanosine, or inosine with a culture of bacteria from the human intestine, from 60 to 100% of the nitrogen in the nucleoside is found to have been converted into ammonia. These results are in harmony with and explain the observation that the urines in ingested nucleic acid are not quantitatively excreted in the form of uric acid, but to a certain extent undergo degradation in the body and are eliminated as urea (doubtless through the intermediate formation of ammonia by the action of the intestinal bacteria).

H. W. B.

#### Fat soluble Vitamins. I. H. STEENBOCK, P. W. BOUTWELL,

and HAZEL E. KENT (*J. Biol. Chem.*, 1918, **35**, 517—526).—Experiments on rats are described, the results of which indicate



that the fat-soluble vitamine in butter-fat is destroyed by heating the butter-fat at 100° for four hours. H. W. B.

**The Changes of Condition in Tissue Colloids Associated with the Healing of Wounds.** W. VON GAZA (*Kolloid Zeitsch.*, 1918, **23**, [i], 1—11).—A discussion of the healing of wounds in the light of modern conceptions of colloid chemistry. E. H. R.

**Indicators in Animal Tissues.** W. J. CROZIER (*J. Biol. Chem.*, 1918, **35**, 455—460. Compare A., 1916, ii, 337).—The hydrozoan *Veella veella*, L., contains a blue pigment which gives an orange extract with 70% alcohol. It is made bright orange by alkalis and decolorised by acids.

Two sponges, "A" and "B," members of the *Aplysinidae*, have yielded coloured aqueous extracts; one is turned bright yellow by acids and blue to purple by alkalis; the other is a crimson-coloured extract, turned violet by acids and yellow by alkalis.

The anterior portion of the oesophagus of the large holothurian *Stichopus moebii*, Semp., contains a reddish-purple echinochrome which is not readily extracted from the tissue. Alkalis intensify the colour; acids change it to bright orange.

By comparing the colour of the natural tissue with the extracted pigment, it is possible to draw some conclusions regarding the degree of acidity or alkalinity of the tissue cells. The tissues of marine animals are in general more acid than the surrounding sea-water, the hydrogen-ion concentration varying between  $p_H=6.0$  and  $p_H=7.6$ , and increasing when death ensues to  $p_H=5$  to 6. Higher alkalinity in the protoplasmic juices of young, rapidly growing individuals has never been observed in these pigmented animals, the normal reaction of the cells concerned being acid rather than alkaline. H. W. B.

**The Phosphorus in Organic Combination in Human Urine. Observation in Acute Yellow Atrophy of the Liver.** JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **89**, 126—134).—Chiefly a review of the literature and of methods. S. B. S.

**The Biochemical Behaviour of Aminomethyl Hydrogen Sulphite.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1918, **89**, 178—180).—Aminomethyl hydrogen sulphite,  $NH_2 \cdot CH_2 \cdot O \cdot SO_3H$  (Reinking, Dehnel, and Labhardt, A., 1905, i, 261), yields formaldehyde in the distillate when an aqueous solution is distilled, and also, but very slowly, when it is kept in water at ordinary temperature. Experiments with urine and meat indicate that it is of little value as an antiseptic. No formaldehyde could be detected in the urine after administration of the acid to a rabbit. When administered to a dog, part appears, from the increase of the neutral sulphur in the urine, to be excreted unchanged. Indican disappears from the urine during administration, and this fact seems to indicate that aminomethyl hydrogen sulphite acts as an intestinal antiseptic. S. B. S.

**The Photolytic and Photodynamic Action of an  $\alpha$ -Furo- $\beta$ -diazole.** P. R. KÖGEL (*Biochem. Zeitsch.*, 1918, **89**, 204—210).

—The substance employed was  $\beta$ -naphthoxadiazole-4-sulphonic acid, which undergoes change on exposure to light. The photodynamic effects were demonstrated on the protozoon *Colpidium colpoda*.  
S. B. S.

**Physiological Action of Hydroatophan.** JULIUS POHL (*Zeitsch. J. exper. Path. Ther.*, 1917, **19**, 198—204; from *Chem. Zentr.*, 1918, i, 929).—Experiments on the frog show that the action of the atophan molecule on the heart is completely altered by hydrogenation and is replaced by a spinal and peripheral excitation. Toxicity towards warm-blooded animals is characterised by increased excitability of the spinal reflexes.  
H. W.

**The Influence of Temperature on the Strength of Action and Surface Activity of Narcotics.** RUDOLF UNGER (*Biochem. Zeitsch.*, 1918, **89**, 238—278).—The influence of changes of temperature on narcotic activity of various substances, such as chloral hydrate, salicylamide, benzamide, monoacetin, and ethyl alcohol, was investigated, the subjects of experiment used being tadpoles, the fish *Leuciscus*, and the sciatic nerve of frogs. In some cases, increase of temperature increased, and in others it diminished narcotic activity. These changes could not always, however, be correlated with changes in the distribution of the narcotic between oil and water, as would follow from the Overton-Meyer theory, or with the change in surface tensions of the solutions. Account has to be taken in investigations of this character of the effect of temperature changes on the general metabolic activity.  
S. B. S.

**Relation between the Chemical Structure of the Opium Alkaloids and their Physiological Action on Smooth Muscle with a Pharmacological and Therapeutic Study of some Benzyl Esters. II. Pharmacological and Therapeutic Study of some Benzyl Esters.** DAVID I. MACHT (*J. Pharm. Expt. Ther.*, 1918, **11**, 419—446. Compare this vol., . 418).—Benzyl acetate and benzoate produce the same effects on smooth muscle as papaverine, but are comparatively non-toxic; they may therefore be employed clinically to alleviate conditions of excessive peristalsis or spasms of viscera containing smooth muscle fibres. Beneficial effects have been observed to follow the administration of one or other of these esters in cases of chronic diarrhoea, dysentery, asthma, etc.  
H. W. B.

**Relations between the Constitution and the [Physiological] Activity of *ac*-Tetrahydro- $\beta$ -naphthylamine and its Derivatives.** ERNST WASER (*Schweiz. Chem.-Zeit.*, 1917, **1**, 12—15; from *Chem. Zentr.*, 1918, i, 830).—Derivatives of *ac*-tetrahydro- $\beta$ -naphthylamine have been examined with the object of

finding one having a quicker and more powerful fever-producing action than the base itself. Experiments undertaken to bring the base into an active, fever-producing form show that in this case Gros's theory, according to which the anæsthetic potential of a salt is proportional to its degree of hydrolytic dissociation, does not hold. There is no appreciable difference in the physiological activity of *ac*-tetrahydro- $\beta$ -naphthylamine and its optically active modifications. The entrance of acyl groups produced a diminution of the activity instead of the expected increase. Whilst the acetyl derivative is much more poisonous to frogs, the converse is the case with warm-blooded creatures (dogs), in which the base itself produces strong dilatation of the pupil and increase of the temperature and the blood-pressure, whilst the acetyl derivative produces contraction of the pupil and a lowering of the temperature and the blood-pressure. A similar behaviour is also shown by the  $\cdot\text{ClO}$ ,  $\cdot\text{COPh}$ ,  $\cdot\text{CO}_2\text{Et}$ ,  $\cdot\text{CO}\cdot\text{NHPh}$ ,  $\cdot\text{CS}\cdot\text{NHPh}$ , and  $\cdot\text{CS}\cdot\text{NHET}$  derivatives. Of the alkyl derivatives, the monomethylated base serves the author's purpose, since in small doses it produces a relatively high feverishness in the shortest time. The ethyl derivative acts like *ac*-tetrahydro- $\beta$ -naphthylamine itself. It has been found that *ac*-tetrahydro- $\beta$ -naphthylamine produces complete immunity against any further injection of itself or of the methyl and ethyl derivatives, that the methyl derivative produces immunity against itself and the ethyl derivative, and that the latter only produces immunity against itself. *N*-Acyl-*N*-alkyl derivatives produce effects which are a combination of those of the mono-substituted derivatives. Thus injection into dogs of *N*-acetyl(or formyl)-*N*-methyl-*ac*-tetrahydro- $\beta$ -naphthylamine produces on the one hand dilatation of the pupil (effect of the methyl derivative) and on the other a lowering of the temperature (effect of the acyl derivative). Experiment shows that a portion of the substance is hydrolysed in the organs (of warm-blooded animals); the resulting methyl derivative or *ac*-tetrahydro- $\beta$ -naphthylamine itself suffices not only to suppress the myotic action of the acyl group, but even to reverse it, but is insufficient to influence the temperature effect. All the results are tabulated.

C. S.

## Chemistry of Vegetable Physiology and Agriculture.

**Problems of Bacteria Adsorption.** H. BECHHOLD (*Kolloid Zeitsch.*, 1918, 23, 35—43).—In the course of a research on the adsorption of bacteria by different materials, experiments were made on the adsorption of certain dyes by the same adsorbents. The basic dye, methylene-blue, was strongly adsorbed by a variety

of substances, such as animal and vegetable charcoal, fuller's earth, bolus, clay, permutite, and silicic acid, whilst trypan-blue, which is acidic, was adsorbed only by charcoal and ferric hydroxide. There is a strong resemblance between the relative adsorptive powers of the above materials for bacteria (*Staphylococcus* and *Bacterium coli*) and for methylene-blue, although ferric hydroxide adsorbs the bacteria and not the colour. Charcoal and fuller's earth surpass any other adsorbent materials, although the mean diameter of their particles may be greater than that of the less adsorbent substances.

E. H. R.

**The Catalase of Bacteria.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **89**, 350—354).—The paper describes attempts to prepare a pure catalase. *Bacillus proteus* was grown on the medium already employed by the author, which contains, besides the inorganic salts, sodium aspartate and sodium lactate. From such cultures, an active catalase could be obtained by precipitation with ammonium sulphate, magnesium sulphate, and sodium chloride. The precipitate obtained was dissolved in water. A catalase could also be precipitated by mercuric chloride; in this case, an active preparation was obtained by redissolving the precipitate in potassium cyanide solution.

S. B. S.

**Chemical Composition and Formation of Enzymes.**  
**XV. Further Experiments with *Bacterium Acidi lactis* (*Streptococcus lactis*).** HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1918, **102**, 176—184. Compare this vol., i, 55, and Euler and Griese, A., 1917, i, 679).—The lactic acid fermentation of lactose by *Streptococcus lactis* is not accelerated, but rather inhibited by sodium dihydrogen phosphate, and in these new experiments an evolution of carbon dioxide has not been observed. The difference between these results and those formerly described (*loc. cit.*), may be due to the employment of a different species of bacterium or to a contamination in the earlier experiments of the bacteria with yeast cells or other micro-organisms. The presence of sodium lactate appears to exert an inhibiting action on the formation of lactic acid by the bacteria.

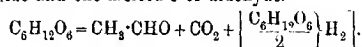
H. W. B.

**The Arrest of Alcoholic Fermentation in the Aldehyde Stage. An Experimental Confirmation of the Acetaldehyde Pyruvic Acid Theory.** CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1918, **89**, 365—414).—Neuberg has shown that yeast contains a ferment which decomposes pyruvic acid into acetaldehyde and carbon dioxide; furthermore, acetaldehyde is readily reduced during yeast fermentations to ethyl alcohol. It seemed therefore probable that acetaldehyde is an intermediate product in alcoholic fermentation. The authors now show that considerable amounts of acetaldehyde can be obtained in the ordinary yeast fermentations of sugars, and can be isolated if the fermentation is

carried out in the presence of sodium sulphite. The equations representing the reactions may be represented as follows:

- (a)  $C_6H_{12}O_6 + Na_2SO_3 + H_2O = C_6H_{12}O_5(OH) \cdot O \cdot SO_2Na + NaOH$ .  
 (b)  $\frac{1}{2}C_6H_{12}O_5(OH) \cdot O \cdot SO_2Na = H_2 + CH_3 \cdot C(OH)(CO_2H) \cdot O \cdot SO_2Na$ .  
 (c)  $CH_3 \cdot C(OH)(CO_2H) \cdot O \cdot SO_2Na_2 = CH_3 \cdot CH(OH) \cdot O \cdot SO_2Na + CO_2$ .  
 (d)  $NaOH + CO_2 = NaHCO_3$ .

As one-half of the molecule should yield aldehyde, which acts as acceptor for the hydrogen evolved, it should not be expected that one molecule of sugar should yield more than one molecule of carbon dioxide and one molecule of aldehyde.



An amount of aldehyde equivalent to 73.45% obtainable on this theory has been obtained.

Full details are given of the methods employed for the quantitative estimation of the aldehyde and alcohol formed during fermentation.

S. B. S.

**Willstätter's Researches on the Assimilation of Carbon Dioxide.** H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 1138—1146).  
 —A review of the recent work of Willstätter on this subject.

A. J. W.

**The Physiological Significance of Potassium in Plants.** TH. WEEVERS (*Biochem. Zeitsch.*, 1918, **89**, 281—282).—A final reply to Stoklasa (*A.*, 1917, i, 682).

S. B. S.

**Active Principles of the Horse Chestnut.** GEORGES MASSOT (*Bull. Sci. Pharmacol.*, 1918, **25**, 65—72; from *Chem. Zentr.*, 1918 ii, 40—41).—Separate examination of the seed capsules and cotyledons has led the author to revise his previous conclusions (*Dis.* Paris, 1910).

The seed capsules yield, after extraction with alcohol, an almost fat-free, bright red residue which gives red needles when crystallised from water; the compound shows tannin reactions, and is transformed by warm sulphuric acid into gallic acid and a red substance.

From the fat-free cotyledons, two acids are obtained: (1) *Aesculic acid*, fine needles, m. p. 214—215°, which are insoluble in water. The salts are yellow and amorphous. The *barium*, *calcium*, *magnesium*, and *lead* salts were investigated. Prolonged boiling of an alcoholic solution of the acid which has been treated with 5% sulphuric acid slowly causes hydrolysis with formation of a reducing sugar. (2) *Aesculinic acid*, golden-yellow, apparently crystalline needles, m. p. 230—231°, laboratory, soluble in water. The *alkali* and *barium* salts are yellow and soluble in water; their solutions have emulsifying properties. The *lead* salt is insoluble in water. The acid is hydrolysed, even by dilute acids, to a reducing sugar and a new acid. The reducing sugars produced from aesculic and aesculinic acids consist of a mixture of mannose and dextrose.

It appears, therefore, that the seed capsules contain a tannin yielding gallic acid. Two glucosidic saponins are present in the cotyledons, of which the insoluble æsculic acid is emulsified by the aqueous solutions of the æsculinic acid; the mixture of acids constitutes the active principle of the seeds, previously termed argyrescin or aphrodescin. If the whole fruit is examined, the presence of the gallic acid of the capsules causes the formation of tannin compounds having properties differing from those of the glucosides.

H. W.

[The Pigment of Myrtle Berries and its Use as an Indicator.] C. MARINI (*Annali Chim. Appl.*, 1918, 10, 32—36).—The pigment of myrtle berries (*Vaccinium myrtillus*, L.) appears to be identical with cœnocyanin, the red colouring matter of wine, to which Glenard (*Ann. Chim. Phys.*, 1858, [iii], 54, 369) assigned the formula  $C_{20}H_6O_2$ , the œnolic acid in which combines with bases to form salts. The pigment of myrtle berries may be extracted with 50% alcohol and precipitated with basic lead acetate. By digesting the washed and dried precipitate, first with ether saturated with hydrogen chloride, then with ether, and finally digesting the insoluble portion with alcohol, and treating the alcoholic extract with ether, a carmine-red pigment is precipitated. This consists of two components, one of which is insoluble in hot water, whilst the other,  $C_{20}H_{14}O_{12}$ , which predominates, is soluble in acidified water, and when boiled with acids is converted into the first component, with the elimination of dextrose. It thus appears to be a glucosidal compound, and is probably a glucotannoid. The pigment extracted from the berries with 90% alcohol acts as a weak acid and forms green salts with alkalis. Test papers, which are more sensitive than turmeric paper, may be prepared from it for use as indicators of acidity or alkalinity. C. A. M.

**Pollen and Pollen Disease. I. Chemical Composition of Ragweed Pollen.** JESSIE HORTON KOESSLER (*J. Biol. Chem.*, 1918, 35, 415—424).—The pollen grains of ragweed (*Ambrosia artemisiifolia* and *A. trifida*), which produce hay fever in certain susceptible persons, contain about 10.5% of water, 10.6% of mineral matter, and 78.9% of organic substances, including 7% of sugars, 10% of lipoids, consisting of fats and phytosterol, and 37% of proteins, crude fibre, etc. The dry pollen contains 4.7% of nitrogen.

H. W. B.

**Absorptive Power of Zeolitic Bases of Soil.** K. K. GEDROITZ (Reprint, pp. 1—55).—Black soil has been treated with 0.2*N.*, *N.*, and 4*N.*-solutions of a number of chlorides, both separately and together, this treatment being repeated until the bases were completely extracted; the results obtained are as follows.

All the zeolitic bases of a soil may be displaced by a certain cation. The bulk of these bases consists of lime (almost 75%), the remainder being magnesia (20%), soda, potash, and possibly manganese oxide. The extraction of soils with hydrochloric acid (about

10%) for the estimation of the zeolitic part gives certain results only for the zeolitic lime, the proportions of the other bases found being too high. Iron and aluminium do not occur in soils—even the red soils of Algeria—as zeolitic bases in detectable proportion.

All the zeolitic bases of a natural soil may be displaced completely by any base either ordinarily present or not in the soil. Except with soils not saturated by bases, the quantity of base absorbed is equivalent to the quantity of bases displaced from the zeolitic part of the soil.

Soil saturated by any base or bases contains this base or bases in the zeolitic part in such quantities as, expressed in equivalents, are independent of the nature of the bases.

The energy of absorption varies with different cations, and is greatest with trivalent and less with bivalent cations; calcium is absorbed more energetically than magnesium. Univalent cations are still more feebly absorbed, sodium more so than potassium.

The relation of the qualitative and quantitative composition of the zeolitic bases of soils to the life of the soil and plant and various other questions are discussed.

T. H. P.

**Saline Soils and their Improvement.** K. K. GEDROITZ (Reprint, pp. 1—16).—The author describes the treatment necessary for the improvement of soils (1) containing an excess of neutral salts, such as the so-called white alkali land, and (2) containing soda, such as the black alkali land.

T. H. P.

**The Inversion of Cane-sugar by Soils and Allied Substances and the Nature of Soil Acidity.** F. E. RICE and S. OSUGI (*Soil Science*, 1918, 5, 333—358).—It is shown that soil of many kinds can cause the inversion of sucrose, this power being a property of the mineral portion as well as of the organic matter of the soil. This effect is due to acid, which may be present as slight amount soluble in the sugar solution or in one of three insoluble forms: (a) acids ordinarily easily soluble, but in the soil strongly adsorbed on the soil particle surfaces; (b) an insoluble acid, such as silicic acid; (c) acid liberated from a neutral salt present in the soil solution by its breaking down, owing to the base being more strongly adsorbed than the acid, this being thus left free to cause inversion of the sugar. Many soils showed inverting action on sucrose in a solution which remained neutral or, in some cases, became alkaline after contact with the soil. Silicate minerals may be given inverting power by submitting aqueous suspensions to a direct current, and soil acidity is increased by a similar treatment of soils. Contrary to previous conclusions, hydrated oxide of lead, copper, bismuth, aluminium, iron, and zinc were not found to have any inverting power.

The authors consider that the measurement of the power of a soil to catalyse the inversion of cane-sugar is probably the only method by which the acidity bound up with the solid phase of the soil can be measured.

W. G.

## General and Physical Chemistry.

**Spectrochemistry and Determination of the Constitution of Tautomeric Compounds.** K. VON AUWERS (*Annalen*, 1918, 415, 169—232).—Brühl showed more than thirty years ago that molecular refraction and dispersion can be utilised to differentiate between enolic and keto-modifications, but the determination in recent times of the composition of keto-enol mixtures by chemical means has frequently led to results which are quite opposed to Brühl's views. The author has undertaken a series of researches, of which this is the first, to ascertain how far spectrochemistry in its present state can be applied to investigations of desmotropic compounds.

With the difference in structure represented by the scheme  $\text{CO}\cdot\text{CHR}\cdot \rightleftharpoons \text{C}(\text{OH})\cdot\text{CR}\cdot$  correspond constant differences in the molecular refraction and dispersion of such magnitudes that a trustworthy decision between the two structures can be made when only homogeneous substances are in question; also the percentage composition of mixtures of simple enols and ketones, for example, a simple unsaturated alcohol and the isomeric aldehyde or ketone, can be ascertained with satisfactory accuracy by the refractometric method, especially if the specific refraction and dispersion are employed instead of the molecular magnitudes. Errors arise, however, and false conclusions may be drawn when certain groups are present in the molecule. For example, in  $\beta$ -diketones,  $\beta$ -ketonic acids, etc., occur the systems  $\text{CO}\cdot\text{CHR}\cdot\text{COR}'$  and  $\text{OH}\cdot\text{C}\cdot\text{CR}\cdot\text{CR}'\cdot\text{O}$ .

The former is spectrochemically normal, but the latter, containing a conjugate system of linkings, exhibits an abnormal increase of the refraction, and still more so of the dispersion. Almost the only possible way of overcoming this difficulty is the calculation of the magnitude of the exaltations by means of known regularities. Eisenlohr and Auwers (*A.*, 1910, ii, 365; 1911, ii, 781) have shown that the magnitudes of the specific exaltations of the refraction and dispersion remain practically constant in compounds containing the same conjugate system, so that 'normal values' of the specific exaltations can be recorded. Unfortunately, this regularity is not equally sharp in all classes of substances, possibly on account of experimental error or of lack of purity of the compounds examined. It is necessary, therefore, to determine more accurately than hitherto the normal values of the specific exaltations for the conjugate systems  $\text{CH}\cdot\text{CH}\cdot\text{CR}\cdot\text{O}$  and  $\text{CH}\cdot\text{CH}\cdot\text{C}(\text{OR})\cdot\text{O}$ , and to ascertain the influence of disturbing substituents on these values. By means of the numbers so obtained, the theoretical values of the molecular refraction and dispersion of the enols could be calculated, and thus the foundations laid for a more trustworthy determination of the equilibrium proportions of enolic and keto-modifications by



means of the optical constants. The author then discusses the values obtained for series of hydroxymethylene compounds and their ethers and esters, and draws the conclusion that a trustworthy calculation of the real molecular refraction and dispersion of enols is possible at the present time only in a few cases in which specially favourable comparison material is available. The following substances have been examined. The percentages are calculated from the spectrochemical data, and the figures in brackets are the percentages found by Meyer's bromine method. Ethyl diacetoacetate, percentage of keto-enol 100 (90—100); acetylacetone, enol 69% (76); methylacetylacetone, keto-enol 38% and 31% in two different preparations (31); ethylacetylacetone, keto-enol about 27%; ethyl acetylmalonate, enol 70% (64); methyl benzoylacetate, enol 25% (16.7); ethyl benzoylacetate, enol 29% (29); ethyl  $\alpha$ -benzoylbutyrate, enol at most a few units per cent.; methylbenzoylacetone, enol 22% (6).

The spectrochemical constants (density and refractive indices for the  $\alpha$ -,  $D$ -,  $\beta$ -, and  $\gamma$ -lines) have been determined of the following hydroxymethylene compounds and their ethyl ethers and acetates;  $\gamma$ -keto- $\beta$ -methyl- $\Delta^2$ -penten- $\alpha$ -ol; hydroxymethylenepinacolin (ethyl ether, b. p. 103—104°/16 mm.; acetate, rhombohedral plates, m. p. 44—45°, b. p. 118—118.5°/16 mm.); 2-hydroxymethylene-cyclohexanone (ethyl ether, b. p. 128.2—128.4°/16 mm.; acetate, b. p. 142—143°/14 mm.); 2-hydroxymethylenementhione; ethyl  $\beta$ -acetoxyacrylate; ethyl  $\beta$ -hydroxy- $\alpha$ -methylacrylate; ethyl hydroxymethyleneacetoacetate; ethyl hydroxymethylenemalonate. The constants are also given for the following diketones and ketonic esters: acetylacetone (and the O-methyl and ethyl ethers); methylacetylacetone; dimethylacetylacetone; ethylacetylacetone; methylbenzoylacetone (and the O-methyl ether);  $\beta$ -methoxy- $\beta$ -amylacrylic acid and its methyl ester; ethyl  $\beta$ -ethoxy- $\beta$ -amylacrylate; ethyl O-acetylacetoacetate; ethyl diacetoacetate; methyl benzoylacetate and the ethyl ester; ethyl ethylbenzoylacetate. C. S.

**Atomic Refraction and Atomic Dispersion of Quadrivalent Lead, Deduced from the Saturated Lead Tetra-alkyls.** GERHARD GRÜTTNER and ERICH KRAUSE (*Annalen*, 1918, 415, 338—362).—Hitherto, the atomic refraction of quadrivalent lead, 17.87 for the red hydrogen line ( $n^2$  formula), has been deduced from only one compound, lead tetra-ethyl. Since it is known that the atomic refraction of silicon, deduced from the silanes, varies between 7.0 and 8.0, it is very desirable that the value for lead should be recalculated, and for this purpose the numerous lead tetra-alkyls prepared by the authors in 1916 and 1917 are well suited, since they are colourless, stable liquids. The values of the atomic refraction and dispersion of quadrivalent lead depend on the number of carbon atoms in the molecule, and increase from the  $C_4$  to about the  $C_{12}$  compounds. The values calculated from the simple, completely symmetrical lead tetra-alkyls ( $PbR_4$ ) increase

regularly with the molecular weight. The authors are decidedly of opinion that there are no constant values. The atomic refraction ( $H_d$  line) increases from 17.07 for the  $C_4$  compound to 18.16 for the  $C_{11}$  compounds, and the atomic dispersions increase from 1.43 to 1.75 ( $H_d-H_e$ ), and from 0.87 to 1.05 ( $H_g-H_e$ ).

Certain regularities in the b. p.'s, densities, and refractions and dispersions of lead alkyls and silicon alkyls are recorded. C. S.

**Atomic Number and Frequency Differences in Spectral Series.** HERBERT BELL (*Phil. Mag.*, 1918, [vi], 36, 337—347).—It has been previously shown by Rydberg and by Kayser and Runge that for elements in the same periodic group the wave-number differences between the components of doublet and triplet series are approximately proportional to the squares of the atomic weights. This relation has been further examined, the atomic weights being replaced by the atomic numbers.

By plotting the square root of the wave-number difference against the atomic number, straight lines are obtained corresponding with the equation  $\sqrt{\nu} = m(N - N_0)$ , in which  $N$  is the atomic number of the element and  $m$  and  $N_0$  are constants. In the first group, the elements lithium, sodium, potassium, rubidium, and cesium fall on one straight line, for which  $m = 0.4447$  and  $N_0 = 1.875$ , whilst potassium, copper, silver, and gold fall on a second straight line, for which  $m = 0.8117$  and  $N_0 = 9.619$ . There is thus a twofold nonlinearity in the first group of the periodic table, and this feature is again met with in the second group.

The linear relation between the square root of wave-number differences and atomic numbers has also been found to hold for the members of other groups in the periodic arrangement.

The logarithmic relation  $\log \nu = p \log N + q$ , which was suggested by Runge and Precht (*A.*, 1903, ii, 346), does not seem to be in better agreement with the facts than the equation  $\sqrt{\nu} = m(N - N_0)$ .

H. M. D.

**Photographic Record of the K-Spectra of Platinum and Iridium.** J. E. LILIENFELD and H. SEEMANN (*Physikal. Zeitsch.*, 18, 19, 269—271).—The K-spectra of platinum and iridium have been examined with the aid of a new type of spectrograph. The intensity distribution in the spectra and the effect of the interposition of a layer of aluminium, as determined by photometric observations, are shown in the form of curves. The photographs obtained show the existence of rays of shorter wave-length than those which have been previously described.

H. M. D.

**Spectrum of Cadmium in the Inactive Gases.** J. N. LILLIE and H. E. WATSON (*Proc. Roy. Soc.*, 1918, [A], 95, 6—120).—Making use of tubes fitted with a cadmium cathode and an aluminium anode, and filled with one of the gases helium, neon, or xenon, the authors have observed certain peculiarities in the spectrum of cadmium. The cadmium lines 6438, 5379, 4808, 5086, 4800, 4678, and 4416 were generally seen, but the

intensity of the lines varied with the pressure and current. Thus with helium at a pressure of 40 mm., four of the cadmium lines were visible, and with neon at 60 mm. pressure, two were visible. In many cases, the lines 5379 and 5338 were entirely absent and the individual lines varied considerably with the gas employed. In the case of the lines 5379 and 5338, it was found that with helium at 40 mm. they were scarcely visible, whilst at 5 mm. they were the brightest lines of the spectrum; in argon they only became visible at 2.5 mm., whilst in xenon these two and 4678 were the only lines visible when a weak current was used. Tables of the intensities of the lines in helium at various pressures are given for the current values 5 and 0.5 amperes. The line 5086 behaved in an unusual manner, in that whilst the experimental conditions were constant, it suddenly flared up to an intensity equal to that of the brightest of the other lines and then suddenly vanished. In the case of argon, the lines 6438, 5086, 4800, and 4678 were very bright at 21 mm. pressure. At 3 mm. pressure, only 5086 was to be seen, and 5379 and 5338 did not appear until the pressure was reduced to 2.5 mm. In krypton, the results were indefinite; the same applies to xenon. The heating effect of the cathode is progressive, being least with helium and greatest with xenon. J. F. S.

**Origin of the Line Spectrum Emitted by Iron Vapour in an Electric Tube Resistance Furnace at Temperatures above 2500°.** G. A. HEMSALECH (*Phil. Mag.*, 1918, [vi], 36, 281—296. Compare this vol., ii, 341).—Further observations on the furnace spectrum of iron at high temperatures are described, all of which point to the conclusion that this spectrum is not a purely thermal effect, but is due to the passage of a current through the vapour of the metal. At 2700°, the furnace spectrum is entirely different from the flame spectrum at the same temperature and approaches in character the arc spectrum of the element. Direct evidence has been obtained that a current will readily pass through the vapour in a tube furnace. The line spectrum does not disappear immediately when the heating current is cut off, but is exhibited for some time afterwards, the lines being extinguished gradually. The spectrum emitted after the current is broken does not correspond with the temperature of the cooling vapour. Attempts to obtain a line spectrum under conditions in which electrical action was excluded by the use of a furnace of special design gave a negative result.

The fact that the vapours of copper, silver, and zinc give no line spectrum when subjected to thermo-electric action in the electric tube resistance furnace at 2700° is supposed to be due to the small conductivity of these vapours as compared with that of the vapours of iron, cobalt, and nickel, all of which readily give a line spectrum under the same furnace conditions.

The methods of excitation which give rise to spectral emission in flames, furnace, arc, and spark are severally distinguished and grouped as (a) thermal, (b) thermo-chemical, (c) chemical.

(d) thermo-electrical, (e) electrical. The observations on iron vapour show that the line spectrum cannot be produced by thermal excitation alone.

H. M. D.

**Ionisation and Spectral Emission of Different Elements in the Positive Column.** O. HARDTKE (*Ann. Physik*, 1918, [iv], 56, 383—387).—According to Stark's investigations, the emission of characteristic spectra is associated with positively charged ions. In consequence of differences in the ionising potentials, it is to be expected that when glow discharge takes place through a tube containing several gases, the positive column will show marked differences in the spectral emission at various points. Experiments made with a tube containing mercury, nitrogen, and argon have actually shown a distribution of the spectra of these elements which are in the order to be expected from a consideration of their ionising potentials. In proceeding from the cathode towards the anode end of the positive column, the order in which the characteristic spectra make their appearance is mercury, nitrogen, argon; this is also the order of the positions of maximum intensity of comparable lines. Of the three elements, mercury has the lowest ionisation potential and argon the highest. The distribution of the spectral emission along the positive column is thus found to be dependent on the ionising potentials of the elements concerned.

H. M. D.

**Binuclear Quinones. Chemical Action of Light.** HANS MEYER and ALFRED ECKERT (*Monatsh.*, 1918, 39, 241—251).—As has already been demonstrated (Meyer and Hofmann, A., 1916, i, 641), dihydroanthracene, when heated, readily decomposes into anthracene and hydrogen, and it is therefore to be expected (Meyer and Hofmann, this vol., i, 383) that the same dissociation should occur under the influence of light. Contrary to the statement of Orndorff and Cameron (A., 1896, i, 176), this substance does undergo chemical alteration when exposed to light from the sun or electric arc, the products being hydrogen and para-anthracene, the latter being formed by the immediate polymerisation of the "nascent" anthracene, which is the primary product; in the presence of substances capable of reacting with the "nascent" anthracene, other products may be obtained. The action of light on anthracene probably also first gives rise to "nascent" anthracene in which the diagonal valency becomes resolved into two free valencies; by these the formation of para-anthracene becomes possible; if oxygen is present, the products are anthraquinone and dihydrodianthrone (compare Luther and Weigert, A., 1905, i, 785), the latter being formed by the further action of light on anthranol, which represents an intermediate stage of the change. It is already known that solutions of benzoquinone and thymoquinone in ethyl alcohol when subjected to light give rise to acetaldehyde and the corresponding quinol. With anthraquinone, however, the quinol derivative is unstable, and in contact with air

regenerates anthraquinone; it is therefore possible to use anthraquinone as a catalyst for the oxidation of ethyl alcohol to acetaldehyde in light, the only other product being a small quantity of an unidentified substance which gives a brown solution in aqueous potassium hydroxide. In a similar manner, isopropyl alcohol can be oxidised to acetone, but methyl alcohol is very stable and is recovered completely unchanged, together with the anthraquinone. This relative stability of methyl alcohol accords well with the earlier result of Meyer and Hofmann (*loc. cit.*), and may account for the preponderance of methyl derivatives amongst the naturally occurring alkyl compounds. 9:10-Dichloro- and 9:10-dibromo-anthracene are unaffected by light, but 10-bromoanthracene in alcoholic solution gradually gives rise to anthraquinone and bromide ions, together with a temporary small deposit of para-anthracene. If dihydroanthracene in acetic anhydride solution is submitted to the action of light, the first deposit of para-anthracene may disappear on prolonged treatment, probably by further oxidation to anthraquinone; anthranyl acetate is obtained as a by-product, its formation supplying an explanation of the origin of dihydrodianthrone in the action of light and air on anthracene in alcoholic solution. Solutions of anthracene in acetic acid, chloroform, and methyl sulphate, when illuminated, give the same products, namely, para-anthracene, anthraquinone, and dihydrodianthrone; it was hoped with the aid of methyl sulphate to isolate anthraquinol in the form of its dimethyl ether, but unfortunately this compound is sensitive to light, and in acetic acid solution is rapidly converted into anthraquinone.

D. F. T.

**The Wave-length of the Hard  $\gamma$ -Rays of Radium.** K. W. FRITZ KOHLRAUSCH (*Physikal. Zeitsch.*, 1918, **19**, 345—349).—The wave-length of the very penetrating  $\gamma$ -rays emitted by radium-B and radium-C is discussed with reference to the absorption of the rays in different elements.

H. M. D.

**The Electrical Conductivity of Salt Vapours.** GERHARD C. SCHMIDT (*Ann. Physik*, 1918, [iv], **56**, 341—362. COMPTE RENDU, 1911, ii, 788; 1913, ii, 747).—Further attempts to obtain reproducible data for the electrical conducting power of salt vapours have given negative results, although various forms of apparatus have been tried with this object in view. The frequently observed fact that the conductivity first increases and then decreases has been traced on the one hand to the slow diffusion of the vapour, and on the other to the caking of the fused salt at the surface, resulting in a reduced rate of vaporisation. The velocities of the positive and negative ions have been determined in the case of cadmium chloride, bromide, and iodide, and of zinc bromide and iodide. Although the results for these different salts are not comparable with one another, they show that the mobility of the negative ions is in all cases greater than that of the positive ions. The ionic mobilities are of the same order of magnitude as those

found by previous investigators for the ions produced in the oxidation of phosphorus and for the ions in flame gases at a considerable distance from the flame. The mobility increases with rise of temperature and depends on the average life of the ion in the sense that the mobility is greater the shorter the average life of the ion.

H. M. D.

#### **New Method for the Determination of Conductivity.**

EDGAR NEWBERRY (T., 1918, 113, 701—707).—Kohlrausch's method for the determination of the electrical conductivity of solutions is criticised, and a method is described which utilises direct current and completely eliminates the effect of polarisation at the electrodes. This method is a simple modification of the method used in the measurement of the resistance of a metallic conductor by observing the fall of potential along it during the passage of a known current. The values obtained for the conductivity of *N*-solutions of potassium chloride and sulphuric acid at 25° are respectively 0.3% greater and 3.6% less than the values recorded by Kohlrausch. In the case of *N*-silver nitrate, the two values are very nearly equal.

H. M. D.

#### **Electrical Conductance of Aqueous Phthalate Solutions.**

HARRISON E. PATTEN, ALFRED J. JOHNSON, and GERALD H. MAINS (*J. Amer. Chem. Soc.*, 1918, 40, 1156—1162).—In reference to the application of potassium hydrogen phthalate as a standard in acidimetry and hydrogen-ion concentration measurements, the authors have measured the conductivity of its aqueous solutions at 25°. The molecular conductivity (corrected for the conductivity of the solvent) was found to increase from 76.9 at  $v=5$  to 153.0 at  $v=10,000$ . Hydrogen-ion concentration measurements gave  $c_H=1.29 \times 10^{-4}$  at  $v=5$  and  $c_H=1.23 \times 10^{-4}$  at  $v=10$ .

The molecular conductivity of normal potassium phthalate is much higher than that of the acid salt, and was found to increase from 184.8 at  $v=20$  to 247.0 at  $v=5000$ .

H. M. D.

#### **Diamagnetism of Hydrogen and the Value of the Magneton.**

A. E. ONLEY (*Proc. Roy. Soc.*, 1918, [A], 95, 58—61).—On the assumption that the molecules of diamagnetic substances contain magnetic elements arranged in such a way that the molecule is self-compensated, so that the application of a magnetic field produces only a diamagnetic effect, it is calculated that the moment of the magneton in the case of hydrogen is equal to  $14.7 \times 10^{-22}$ , which agrees closely with the moment for molecules of ferromagnetic and paramagnetic substances ( $16.5 \times 10^{-22}$ ). If each hydrogen atom contains one magneton, the calculated radius of the electron orbit is about  $1 \times 10^{-8}$  cm.

H. M. D.

**The Coefficients of Magnetisation of Oxygen and of Nitric Oxide, and the Theory of the Magneton.** EDMOND BACER, PIERRE WEISS, and AUGUSTE PICCARD (*Compt. rend.*, 1918, 187, 484—487).—The authors have made fresh measurements of

the coefficients of magnetisation of oxygen and nitric oxide by three different methods, the values obtained being: for oxygen,  $\chi_{20} = 1.077 \times 10^{-4} \pm 0.003 \times 10^{-4}$ ,  $\sigma_{O_2} = 1.587 \times 10^4$ ; for nitric oxide,  $\chi_{20} = 0.487 \times 10^{-4} \pm 0.0025 \times 10^{-4}$ ,  $\sigma_{NO} = 1.033 \times 10^4$ . These values are in contradiction with the theory of the magneton, and it is suggested either that oxygen and its compounds are an exception to the general law or that the discrepancies are due to a difference between the kinetic theory and experimental facts. W. G.

**Magnetic Susceptibility of Mixtures of Liquids.** ALPHRED W. SMITH and ALVA W. SMITH (*J. Amer. Chem. Soc.*, 1918, 40, 1218—1224).—Quincke's method has been used in the investigation of the magnetic susceptibility of mixtures of acetone and water, acetic acid and water, acetic acid and benzene, and acetone and ethyl alcohol. Within the limits of experimental error, the results obtained for the four pairs of substances are in agreement with the requirements of the additive law. It is suggested that the magnetic susceptibility may advantageously be used in the analysis of binary mixtures. H. M. D.

**The Causes of Abnormal Boiling Points.** A. BERTHOUD (*J. Chim. Phys.*, 1918, 16, 245—278).—A theoretical discussion in which the author shows that de Forcrand's views as to the relationship of the abnormal boiling points of water, hydrofluoric acid, and ammonia to their heats of formation and their molecular dissymmetry (compare this vol., ii, 107) are not in accord with experimental facts. On the other hand, molecular association has the effect of raising the boiling point, but not to the extent often stated. Calculations founded on the additivity of the constants  $k$  and  $\sqrt{a}$  (compare van Laar, A., 1916, ii, 610) indicate that amongst the substances studied, acetic acid is the only one of which the boiling point and the critical temperature can be explained entirely by association. In cases such as those of water, alcohol, and ammonia, another factor intervenes. The critical pressures of the last-named compounds are also too high, and this cannot be explained on the grounds of molecular association. This other factor, which works with the molecular association in causing high boiling points and critical temperatures in the cases of water and the alcohols, lies in the particularly high value of the constant  $k$  independent of the molecular association, in substances containing an -OH group. W. G.

**Freezing Points of Concentrated Solutions and the Free Energy of Solution of Salts.** WORTH H. RODEBUSCH (*J. Amer. Chem. Soc.*, 1918, 40, 1204—1213).—Recent improvements in the method of determining the freezing points of dilute solutions (Adams, A., 1915, ii, 222) have been made use of in the investigation of concentrated solutions, the relation between the freezing point and the concentration of various aqueous salt solutions having been followed down to the eutectic temperature. The following

data are recorded for the eutectic composition (grams anhydrous salt per 100 of water) and the eutectic temperature: sodium chloride, 30.4, 21.12°; potassium chloride, 24.60, 10.66°; ammonium chloride, 24.50, 15.36°; magnesium chloride, 28.00, 33.50°; calcium chloride, 48.00, 51.0°; potassium bromide, 45.65, 12.60°; sodium nitrate, 62.50, 17.46°; ammonium nitrate, 74.80, 16.67°; ammonium sulphate, 66.40, 18.34°. Temperature measurements were made by the aid of a copper-constantan thermocouple.

The thermodynamic equations required for the calculation of the free energy change which accompanies the formation of solutions of different concentrations are considered and applied to the experimental data for solutions of sodium chloride and potassium chloride.

H. M. D.

### Representation of the Properties of Binary Systems.

G. MASING (*Int. Zeitsch. Metallographic*, 1917, 9, 82—89; from *Chem. Zentr.*, 1918, i, 800—801).—In the graphic representation of the properties of binary systems in relation to the composition, curves of the most peculiar form can, in certain cases, be obtained by a quite justifiable selection of the independent variables, and from these curves quite unjustifiable conclusions can be drawn. The selection of the variables, therefore, is not immaterial. As composition variable, an additive property such as mass (weight or atomic-percentage) is suitably selected. The selection of volume percentage, for example, gives complicated curves, on account of volume changes; in electrical conductivity, such a selection would represent the relation between conductivity, composition, and specific volume, instead of the relation between conductivity and composition.

Likewise, the property function ought to be so selected that it is additive for a mechanical mixture. Two principal cases are to be differentiated in the case of alloys. When the property under examination is a purely intensity magnitude, it is independent of the quantity of the phases present, and for a mechanical mixture is represented by a straight line parallel to the concentration axis. In the second case, when the property is a specific magnitude, that is, is calculated on unit quantity of the alloy, this unit must always be the same as that employed in plotting the concentration axis. For example, the specific volume is correctly represented as a function of the weight concentration, but it is incorrect to represent the density as a function of the weight percentage.

The author discusses the representation of density, specific volume, atomic volume, electrical conductivity, and the phenomena of fusion and transition.

C. S.

**The Fluidity and Specific Volume of Binary Liquid Mixtures.** W. HERZ (*Zeitsch. anorg. Chem.*, 1918, 104, 47—52). Compare this vol., ii, 155).—Mixtures of methyl alcohol and ethyl alcohol and of methyl alcohol and propyl alcohol show a linear relationship between fluidity (expressed in C.G.S. units) and



specific volume. In the case of ethyl alcohol-propyl alcohol mixtures, however, the linear relationship no longer holds, and the curves for mixtures of water with methyl and ethyl alcohols both show a well-marked minimum with approximately 40% alcohol. A number of other mixtures show a linear relationship, for example, trichloroethylene and pentachloroethane, tetrachloroethylene and carbon tetrachloride, tetrachloroethane and carbon tetrachloride, propyl acetate and amyl formate, chlorobenzene and bromobenzene at 12° and 64°, acetic acid and formic acid. E. H. R.

**Surface Deconcentration.** L. BERZELLER (*Kolloid Zeitsch.*, 1918, 23, 31—35).—Measurements have been made of the surface tension of aqueous solutions of phenol, valeric acid, thymol, and hæmoglobin in presence of varying quantities of different alcohols, the object being to determine to what extent the depression of the concentration of the solute at the surface of the solution by the alcohol is dependent on the concentration of the latter. The surface tension measurements were made by means of a Traube stalagmometer, the drop-numbers being taken for convenience as a measure of the surface tension. As a measure of the surface deconcentration, the difference,  $\Delta$ , between the drop-number of the solution containing both alcohol and solute under examination and that of a solution containing alcohol alone is taken.

The influence of the concentration of ethyl, propyl, and isoamyl alcohols on aqueous solutions of phenol is expressed by the equation  $(\Delta^2/\sqrt{P^2})/\sqrt{D} = \text{const.}$ , where  $P$  is the concentration of the alcohol and  $D$  is proportional to the lowering of the surface tension of water by alcohol of concentration  $P$ . In the case of methyl alcohol, however, a better constant is obtained if, in the above equation,  $D$  is substituted for  $\sqrt{D}$ . The effect of the four alcohols on aqueous solutions of valeric acid and thymol, respectively, is satisfactorily represented by the original equation, although in the case of thymol at high concentration of alcohol the expression no longer holds. In the case of hæmoglobin, the constancy of the expression is restricted to still smaller ranges of concentration of alcohol. It is noteworthy that for each of the four solutes examined, the constants found for the alcohols, methyl, ethyl, propyl, and isoamyl, are always in the same proportion, approximately 5:4:3:1. Further, when the constants found for each alcohol are divided by the factor  $D_0$ , the lowering of the surface tension of water by the solute examined, constants are obtained which are characteristic for the different alcohols and almost independent of the character of the solute. E. H. R.

**Adsorption by Hide-powder.** II. VÁCLAV KUBELKA (*Kolloid Zeitsch.*, 1918, 23, 57—63. Compare A., 1916, ii, 297).—Observations on the adsorption of hydrogen chloride from aqueous solutions by hide-powder are described. Over a period of two years, the hide-powder was found to have the same adsorption capacity. From pure aqueous solutions of hydrogen chloride, the quantity of

this which is adsorbed by the hide-powder is independent of the concentration of the solution. In presence of considerable quantities of sodium chloride, this relation no longer obtains. The adsorption in these circumstances increases with the concentration of the acid, and the form of the adsorption curve suggests that the phenomenon is of complex character. It seems probable that the first portions of acid which are removed from solution combine with the hide-powder to form a definite chemical compound. This compound appears to contain about 977 grams of hide-powder per gram-molecule of hydrogen chloride. This number agrees fairly closely with those which have been previously obtained for the molecular weight of gelatin. The further removal of hydrogen chloride from solution takes place in agreement with the usual adsorption formula. It thus appears that there are two distinct processes involved in the so-called adsorption of hydrogen chloride by hide-powder. [Compare *J. Soc. Chem. Ind.*, 665A.]

H. M. D.

**The Rate of Capillary Ascension of Liquids.** RICHARD LUCAS (*Kolloid Zeitsch.*, 1918, 23, 15—22).—From Poiseuille's expression for the rate of flow of liquids in capillary tubes, the author has deduced the expression, for the rate of ascension of a liquid in a capillary tube,  $h^2 = \omega / \eta \cdot r / 2 \cdot \cos d \cdot t$ , where  $h$  is the height to which the liquid rises in time  $t$ ,  $\omega$  the surface tension,  $\eta$  the viscosity,  $r$  the radius of the tube, and  $d$  the meniscus angle. This formula is identical in form with Ostwald's empirical formula,  $h^{1/m} = kt$ , if  $m$  is made = 0.5. Experiments have been made on the rate of ascension of a number of liquids in filter-paper, the liquids used being glycerol, aniline, nitrobenzene, benzene, methyl and ethyl alcohols, ether, chloroform, carbon tetrachloride, and carbon disulphide. Three grades of filter-paper were used of widely differing porosity, and in every case the results were satisfactorily expressed by Ostwald's equation, the value of  $m$ , however, being always less than 0.5 but greater than 0.4. If  $k$  is expressed in absolute units, the equation can be written  $k\eta/\omega = r/2 \cdot \cos d \cdot t = \text{const.}$  The value of this constant is independent of the liquid used and is proportional to the mean diameter of the pores of the paper. The values of this constant obtained from the different liquids for each paper agreed satisfactorily, the ratios of the porosities of the three papers used being found to be 1:4:12.5.

It is to be observed that the formula  $h^2 = \omega / \eta \cdot r / 2 \cos d \cdot t$ , being an approximation, is only strictly true when the capillary rise is still far from completion, that is, when  $h$  is small compared with  $\frac{2\omega}{r \cos d}$ , the maximum rise. The formula cannot therefore be expected to hold for glass capillaries, in which the rate of ascension is very rapid.

E. H. R.

**Theory of the Osmosis and Ultra-filtration of Colloidal Solutions.** WOLFGANG OSTWALD (*Kolloid Zeitsch.* 1918, 23, 78).—Although the constituents of a colloidal solution appear to be separable by the expenditure of less energy than is required

for the separation of solute and solvent in the case of a molecular solution, this is entirely due to the difference in the order of magnitude of the "molar" concentration of the solutions which are compared.

The methods employed in the filtration of colloidal solutions are discussed, with particular reference to the mechanical efficiency of the filters. In comparing the behaviour of colloidal solutions in respect of ultra-filtration, it is necessary to distinguish between those portions of the dispersive medium which are associated with the disperse phase in different forms. H. M. D.

**Abnormality of Strong Electrolytes. III. The Osmotic Pressure of Salt Solutions and Equilibrium between Electrolytes.** JNANENDRA CHANDRA GHOSH (T., 1918, 113, 707—715).—By application of Clausius's virial theorem to salt solutions, it is shown that the author's theory (compare T., 1918, 113, 449, 627) leads to the relation  $i = n\{1 - \frac{1}{2} \log_e 1/a\}$ , where  $i$  represents the osmotic ratio,  $n$  the number of ions resulting from a molecule of the salt, and  $a$  the activity coefficient.

By comparing the values of  $i$  for binary and ternary electrolytes which are derived from freezing-point observations with those which are calculated (1) from the above equation, and (2) from the Arrhenius equation  $i = 1 + (n-1)\alpha$ , it is shown that the equation based on the Clausius theorem and the author's theory of electrolytes is in better agreement with the experimental results. The failure of the Arrhenius equation is very strongly marked in the case of ternary electrolytes.

It is shown that no change in the activity coefficient occurs when salt solutions of the same equivalent concentration are mixed together. H. M. D.

**Rhythmic Diffusion Structures in Gelatin-Salt Jellies.** III. W. MOELLER (*Kolloid Zeitsch.*, 1918, 23, 11—15. Compare this vol., ii, 301).—In connexion with his theory of jelly structure the author has made experiments with textile fabrics which indicate how, by the displacement of superposed layers of an ultramicroscopic lattice structure, rhythmic macroscopic effects may be produced. The development of a spheritic structure when hydrochloric acid is allowed to diffuse into a semi-liquid gelatin jelly containing sodium chloride is supposed to be caused by some such displacement of the lattice structure of the gelatin accompanied by hydrolytic fission, the resulting rhythmic structure being subsequently rendered visible by deposition of colloidal particles. E. H. R.

**Experiments in Rhythmic Banding.** HARRY N. HOLMES (*J. Amer. Chem. Soc.*, 1918, 40, 1187—1195).—Silicic acid gels have been found to exhibit well-developed rhythmic banding effect when suitable electrolytes are dissolved in the gel, which is then brought into contact with aqueous solutions which react with the

an electrolyte to form insoluble compounds. Banded precipitates have thus been obtained of mercuric iodide, metallic gold, copper chromate, basic mercuric chloride, cuprous oxide, copper ferrocyanide, and basic lead iodide. The best results were obtained in the case of copper chromate, the bands and the intervening clear spaces being very sharply defined.

The formation of the rhythmically distributed bands is explained in terms of differences in the rate of diffusion. If the gel contains chromate ions and the aqueous solution copper ions, then the latter diffuse into the gel and a layer of copper chromate is formed at the surface of the gel. The chromate ions below this precipitation zone diffuse into the region which is now depleted of chromate ions and meet the advancing copper ions, whereby the thickness of the precipitation layer is increased. The difference in concentration of the chromate ions in contiguous layers is greatest just below the front of the thickening band, and in consequence the copper ions have to advance some distance beyond the band before the concentration of chromate ions is sufficiently large to cause precipitation of copper chromate and the formation of a new band. These conditions are repeated, with the production of precipitation zones in rhythmic distribution.

H. M. D.

**Isomorphous Mixtures.** PAUL GAUBERT (*Compt. rend.*, 1918, 167, 491—494).—From a general study of the properties of crystals deposited from solutions of mixtures of isomorphous salts, the author considers that the expression solid solution must be reserved for crystals, which are stable, perfectly homogeneous, and, in the case of coloured salts, almost without polychroism. Crystals formed by the regular association of very small crystals, and even in certain cases by crystalline particles themselves, must be regarded as mixed crystals.

W. G.

**The Retardation of the Formation of Prussian Blue in Aluminium Hydroxide Sols.** H. FREUNDLICH and J. REITSTÖTTER (*Kolloid Zeitsch.*, 1908, 23, 23—24).—Polemical in reply to Vorländer, this vol., ii, 301.

E. H. R.

**Effect of Dissolved Substances on the Velocity of Crystallisation of Water.** III. ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, 40, 1168—1184. Compare A., 1916, ii, 233, 424).—Further observations have been made on the influence of dissolved substances on the rate of crystallisation of water at a constant temperature of  $-7.0^{\circ}$ . From the results obtained with metallic chlorides and sulphates, alcohols and other related organic compounds, sugars and colloids, it would seem that the retarding influence of the dissolved substance is mainly determined by its degree of hydration. If the substances examined retard the crystallisation with the exception of colloidal ferric hydroxide, which at concentrations of 1—20 grams per litre produces an increase in the rate of crystallisation. The effects observed point to the conclusion that substances which form crystallo-hydrates are hydrated in solution to

a greater extent than similar substances which crystallise in the anhydrous form. In support of the view that the velocity of crystallisation depends on the degree of hydration of the solute, a distinct parallelism is found between the velocity and the heat of solution.

Experiments made with water and potassium chloride solutions in tubes of different kinds show that the velocity of crystallisation varies directly with the diameter of the bore, but is independent of the thickness of the wall of the tube.

It is supposed that the effects produced by dissolved substances are specific in nature, but it is not yet possible to calculate from these the absolute degree of hydration.

H. M. D.

**Effect of Dissolved Substances on the Velocity of Crystallisation of Formamide.** ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1184—1187).—Formamide is very susceptible to spontaneous crystallisation when but slightly undercooled, but it has been found possible to compare the influence of various alkali haloids on the velocity of crystallisation at  $-2.5^{\circ}$ , which corresponds with an undercooling of  $4.75^{\circ}$ . The retardation of the crystallisation is supposed to be due to solvation, the extent of which appears to run parallel with the degree of hydration in aqueous solution.

For the same degree of undercooling, the velocity of crystallisation of formamide is only about one-seventh of the velocity found for water. The difference in the rates is supposed to be connected with the greater extent to which formamide is associated.

H. M. D.

**The Chemical Kinetics and Constitution of Aqueous-alkoholic Solutions of Sodium Alkylloxides.** RUD. WEGSCHEIDER (*Monatsh.*, 1918, **39**, 201—218).—A mathematical discussion of the kinetics of chemical changes between a solution of sodium in aqueous alcohol and substances which react with both sodium hydroxide and sodium ethoxide. The assumption of Lobry de Bruyn and Steger (*A.*, 1899, i, 745; see also Senter and Wood, *L.*, 1915, **107**, 1070), that the ratio between the amounts of sodium hydroxide and sodium ethoxide can be directly deduced from the relation between the quantities of the two reaction products, is erroneous, as also is therefore their conclusion that even in 50% alcohol the sodium is present mainly as sodium ethoxide.

D. F. T.

**Alkaline Saponification. Esterification of Citric Acids and their Glycerides.** J. PINNOW (*Zeitsch. Elektrochem.*, 1918, **24**, 270—278).—The author shows that, contrary to the statement of Meyer (this vol., ii, 223), his accounts of the esterification of triethyl citrate and the hydrogen ethyl citrates constitute the first complete work on the step-wise alkaline hydrolysis of esters of a tribasic acid. The work previously published (this vol., ii, 146) is continued in the present paper. It is shown that cotton-seed

oil when treated with cold alcoholic potash is converted to the extent of 75% into the ethyl ester, whilst a small quantity is directly hydrolysed. The glycerol content in cotton-seed oil can be estimated by weighing and the use of an analytical correction. Asymmetric diethyl hydrogen citrate is hydrolysed in two ways by dilute acids. It is also shown that in preparing diethyl esters from the monoethyl esters obtained by the hydrolysis of triethyl citrate, the asymmetric diethyl ester is produced in the larger quantity. A comparison of the velocity of hydrolysis of the glycerides of acetic acid and other esters shows that the complex formation between the alkali or alcoholate does not take place with the whole ester molecule, but with dissociated groups.

J. F. S.

#### Atomic Structure from the Physico-chemical Standpoint.

ALFRED W. STEWART (*Phil. Mag.*, 1918, [vi], 36, 326—336).—The question of the structure of the atom is considered more particularly with reference to the chemical properties of the elements, and a model atom is described which takes account of the following facts: (1) the independence of the  $\alpha$ - and  $\beta$ -ray changes, (2) the difference in origin of the electrons which are involved in ordinary chemical changes and those which are ejected during  $\beta$ -ray changes, (3) the impossibility of controlling the ejection of  $\beta$ -ray electrons by any known process, (4) the alteration of the atomic number by either an  $\alpha$ - or a  $\beta$ -ray change, (5) the production of helium in an  $\alpha$ -ray change, (6) the difference in degree between the effects produced by the ejection of a  $\beta$ -ray and the corresponding change in valency produced by chemical means, (7) the possession of the same chemical properties by atoms of different weights, and, on the other hand, the identity of the weights of atoms which have different chemical properties. In this model atom, the core is negative and consists of a group of negative electrons travelling in closed orbits. Closely surrounding these are the orbits occupied by positive electrons, some of which are supposed to be associated with negative electrons. The mass of the atom is supposed to be concentrated in this zone. Further from the core, other negative electrons move in orbits of an elliptical character, the ellipses being much elongated, so that the electrons travel in paths comparable with those of comets in the solar system. When these "cometary" electrons are in a position of aphelion to the nucleus, they will be moving relatively slowly in their orbits, and hence will be less resistant to forces tending to remove them from the atom. The forces attracting the electrons towards the nucleus will also be weakest in this position, and the ease with which the valency of certain elements can be altered by chemical or electrical means can thus be readily explained. Elements which show no changes of valency may be assumed to have more nearly circular orbits for the electrons in the outer zone of the atom. For the interpretation of other properties the original must be consulted.

H. M. D.

**Romance of the Chemical Elements, their History and Etymology.** INGO W. D. HACKH (*Amer. J. Pharm.*, 1918, 90, 478—492, 565—579).—An account of the history and the etymology of the elements. Chronological tables and family trees of related elements serve to illustrate the historical description.

H. M. D.

**Modification of the Periodic Table.** INGO W. D. HACKH (*Amer. J. Sci.*, 1918, [iv], 46, 481—501).—A more ample account of work already published (this vol., ii, 306).

C. S.

**Definition of Valency.** F. H. LORING (*Chem. News*, 1918, 117, 319—322).—A general discussion of the meaning to be applied to the term valency. Valency is described as of four types: (1) that existing with helium atoms acting as subatomic units; this is a stronger type of valency, and consequently stronger affinity; (2) that involved in atomic combinations, that is, the ordinary valency, but with affinities which are not correlated to the valency values; (3) a residual or excess valency, which tends to become diffuse and is exerted in the formation of molecular complexes; and (4) a more remote type of valency, which, being wholly diffuse, is more of the nature of an affinity pure and simple, and in this case, which is active in cohesion, the idea of valency may be eliminated. The author supports his suggestions by extracts from various writers.

J. F. S.

**Further Contributions to the Life-history of Johann Rudolph Glauber.** WALTER BRIEGER (*Chem. Weekblad*, 1918, 15, 984—987).—A popular account, with portrait, of the life of Glauber.

A. J. W.

## Inorganic Chemistry.

**Hydrogen Sulphide Generator.** T. R. ERNEST (*J. Amer. Chem. Soc.*, 1918, 40, 1224—1226).—A compact form of generator with concentric compartments for the iron sulphide and the acid. Ease of control, absence of leakage, and large storage capacity are advantageous features claimed for the author's design.

H. M. D.

**Method of Handling Phosphorus.** BERTRAM BLOUNT (*Analyst*, 1918, 43, 291—292).—Phosphorus may be safely handled in a vessel filled with nitrogen free from oxygen. Carbon dioxide gas cannot be used for this purpose, since, should the phosphorus take fire, it will continue to burn, decomposing the gas.

C. A. M.

**Electrolysis of Molten Sodamide and Potassamide.**

LOTHAR WÖHLER and F. STANG-LUND (*Zeitsch. Elektrochem.*, 1918, **24**, 261—270).—An open apparatus is described in which pure sodamide and potassamide may be prepared by the action of ammonia on the molten metals. The apparatus is so constructed that the physical constants of the product may be determined immediately after preparation, and the purity thereby determined. Melting points of the products were obtained from cooling curves, and the values, sodamide, m. p.  $210^{\circ}$ , potassamide, m. p.  $338^{\circ}$ , obtained, instead of the values  $149\text{--}155^{\circ}$  and  $270\text{--}272^{\circ}$ , respectively, which had been obtained previously by Titherley (T., 1894, **65**, 504). Apart from the breaks occasioned in the cooling curves by the solidification of the amides, no other breaks were observed. The method of analysis of the amides proposed by Dennis and Browne (A., 1904, ii, 558) is modified by moistening the amide with alcohol before its decomposition by water. This has the effect of making the decomposition occur more regularly. The molten amides conduct a current electrolytically, due to the ionisation  $\text{NaNH}_2 \rightleftharpoons \text{Na}^+ + \text{NH}_2^-$ . Hydrazine is not formed at the anode as was expected, but ammonia and nitrogen, the discharge of the anion taking place according to the equation  $6\text{NH}_2^- + 6\text{H}^+ = 4\text{NH}_3 + \text{N}_2$ . The expected formation of hydrazine was probably prevented by the catalytic action of the sodamide. Chlorine and iodine do not form hydrazine with the amides, but halogen-substituted ammonias. The specific conductivity has been determined, and the values  $\kappa_{250^{\circ}} = 0.593 \text{ ohm}^{-1}$  for sodamide and  $\kappa_{400^{\circ}} = 0.389 \text{ ohm}^{-1}$  for potassamide, obtained. The decomposition voltage at the melting point is found to be 0.71 volt for sodamide and 0.87 volt for potassamide, the former having a temperature coefficient  $1.52 \times 10^{-3} \text{ volt}$ . J. F. S.

**Alteration in Concentrated Solutions of Sodium Hypochlorite.** M. BOUVET (*Bull. Sci. Pharmacol.*, 1917, **24**, 347—349; from *Chem. Zentr.*, 1918, i, 941).—Concentrated solutions of sodium hypochlorite rapidly lose their activity in direct sunlight. Decomposition occurs most readily in white glass flasks, considerably more slowly in vessels of brown glass. Solutions preserved in the shadow or in the dark are practically unchanged after four weeks. H. W.

**Microchemical Reactions of Metals with Rubidium and Cæsium Chlorides.** JAN VERMANDE (*Pharm. Weekblad.*, 1918, **55**, 1131—1134).—An account of the preparation of double chlorides of cæsium and rubidium with mercury, silver, copper, bismuth, antimony, tin, lead, nickel, cobalt, cadmium, iron, zinc, manganese, and magnesium. These chlorides are analogous to the corresponding double salts of potassium and sodium. No double chlorides were obtained containing arsenic, aluminium, calcium, strontium, barium, potassium, sodium, or lithium. A. J. W.



**Silver Arsenide. I. Attempt to Reduce Silver Arsenate by Formaldehyde.** ENRIQUE V. ZAPPI and JUAN L. LANDAUER (*Bull. Soc. chim.*, 1918, [iv], 23, 318—322).—Attempts to reduce silver arsenate either in the solid state or in hot or cold ammoniacal solution with formaldehyde were not successful. The product from the latter method oscillated in composition around that expressed by the formula  $2Ag_3AsO_4, Ag$ . W. G.

**Thermal Decomposition of certain Inorganic Trinitrides.** ARTHUR R. HITCH (*J. Amer. Chem. Soc.*, 1918, 40, 1195—1204).—The possibility of regulating the decomposition of metallic trinitrides, when heated, has been examined in experiments conducted at different temperatures. Silver, mercurous, mercuric, barium, and thallous trinitrides decompose quickly into the corresponding elements when the temperature is suitably adjusted, but the behaviour of lead, cupric, and ammonium trinitrides is not so easily controlled. In the case of silver trinitride, which was more closely examined, quiet decomposition occurs at 280—290°. The rate of decomposition was found to increase with the temperature, and in a vacuum the evolution of nitrogen was much more rapid than at atmospheric pressure.

An arrangement of apparatus is described in which the thermal decomposition of the trinitrides may be quantitatively determined, and it is proposed to make use of this in the determination of the atomic weight of nitrogen. H. M. D.

**An Impurity of Zinc Dust.** O. BINDER (*Chem. Zeit.*, 1918, 42, 458).—Zinc dust frequently contains a considerable amount of chlorine, and should be proved free therefrom before being used for reductions in analytical work. C. A. M.

**Basic Carbonate of Copper.** HORACE BARRATT DUNNICLIFF and SUDARSHAN LAL (*T.*, 1918, 113, 718—722).—The statement that commercial copper carbonate has the same composition as malachite is not in agreement with the authors' results for thirteen samples which have been examined. Attempts to prepare a basic copper carbonate of approximately constant composition have shown that a substance of the composition  $2CuCO_3, 5Cu(OH)_2$  may be obtained by the action of a mixture of sodium carbonate and sodium hydrogen carbonate on copper sulphate solutions.

H. M. D.

**The Rare Earths. VII. Separation of Holmium.** L. F. NYTEMA and B. S. HOPKINS (*J. Amer. Chem. Soc.*, 1918, 40, 1163—1167).—Experiments made with rare earth fractions containing only holmium and yttrium indicate that these may be separated by fractional hydrolysis of the phthalates. By gradually raising the temperature of the phthalate solution, basic phthalates are precipitated, and the first fractions are found to contain a larger proportion of holmium than that present in the original rare earth mixture.

Fractional precipitation by sodium nitrate from a dilute neutral nitrate solution also leads to an accumulation of holmium in the first fractions. A holmium-yttrium mixture with an "atomic weight" equal to 97.7, when separated into six fractions by this method, gave 103.3 for the "atomic weight" of the metal in the first fraction and 91.3 in the last fraction. The nitrite method is considered to promise better results than the phthalate method.

H. M. D.

### Fusion and Crystallisation of Iron-Carbon Alloys.

RUDOLF RUER and FRANZ GOERENS (*Ferrum.*, 1917, 14, 161—177; from *Chem. Zentr.*, 1918, i, 907. Compare Ruer and Iijin, *A.*, 1911, ii, 494; Ruer and Goerens, *A.*, 1916, ii, 483; 1917, ii, 474).—With the object of reinvestigating certain portions of the equilibrium diagram of iron-carbon alloys, the authors have melted pure electrolytic iron with sugar carbon in an electric furnace in porcelain tubes in an atmosphere of nitrogen. The melting points of antimony (630.6°), copper (1084°), and nickel (1451°) were used for the calibration of the thermometer. The mean of the melting and solidifying points of the cementite eutectic is found to be 1145°, that of the graphite eutectic 1152°; the former alloy contains 4.2% and the latter 4.15% of carbon. The perlite point occurs at 721° with 0.9% of carbon. The authors draw the conclusion that the formation of graphite in grey pig iron occurs in the liquid phase, and that the substance separates as such from the molten mass and is not formed by the disintegration of other pre-formed crystalline varieties.

A résumé of the data which are necessary for the construction of the melting-point curves is appended.

H. W.

### High Temperature Investigations. XI. Chromium and Carbon.

OTTO RUFF and THEODOR FOHRER (*Zeitsch. anorg. Chem.*, 1918, 104, 27—46).—An account of a detailed study of the alloys of chromium and carbon. Alloys saturated with carbon were prepared by melting chromium (prepared by the aluminothermite process and containing Al 1.33%, Fe 0.62%, Si 0.26%,  $Al_2O_3$  0.53%) in a crucible of pure carbon at temperatures varying from 1840° to 2567° for fifteen minutes, stirring frequently with a carbon rod. Samples less rich in carbon were obtained by melting a mixture of chromium and a finely powdered alloy containing 11.16% of carbon in a magnesia crucible at 1800—1850°. At higher temperatures, chromium attacks the crucible. Alumina or zirconia is no more resistant than magnesia. For the analysis of the alloys, special methods were devised, consisting in oxidising by means of potassium nitrate or sodium peroxide, carbon and chromium being converted, respectively, into carbonate and chromate.

The alloys of carbon and chromium fall into two groups: (1) those containing up to 8.5% of carbon, completely soluble in hot 24% hydrochloric acid; (2) those containing more than 8.5% of carbon, partly soluble in the same acid.

The alloys of the first group, which have been prepared containing 1.51% to 8.49% of carbon, when repeatedly extracted with cold 2*N*-hydrochloric acid until no more chromium dissolves, leave a residue of practically pure  $\text{Cr}_5\text{C}_2$ . The low carbon alloys show a close fracture, those with a higher carbon content being coarser and showing distinct crystalline needles. Microscopic sections etched with hydrochloric acid (no other etching reagent is applicable to these alloys) show crystals of the compound embedded in a eutectic. The alloy containing 8.49% of carbon is practically pure  $\text{Cr}_5\text{C}_2$  and contains no eutectic, the section showing a uniform mass of crystals. The carbide,  $\text{Cr}_5\text{C}_2$ , which can be prepared in quantity, forms silvery crystals,  $D_4^{20} = 6.915$ , *m. p.*  $1665^\circ$ . It is not attacked by aqua regia, and on melting undergoes no appreciable decomposition. No trace of the compound  $\text{Cr}_4\text{C}$  described by Moissan was found.

The alloys of the second group, containing more than 8.5% of carbon, contain no free chromium, only carbide and graphite. The carbon content of the saturated alloys increases with the temperature of preparation, from 12.42% at  $1840^\circ$  to 14.03% at  $2233^\circ$ , and more rapidly to 23.12% at  $2567^\circ$ . When treated with hot 24% hydrochloric acid, part of the alloy dissolves, the ratio of chromium to carbon dissolved indicating that the soluble carbide has the composition  $\text{Cr}_3\text{C}_2$ . The existence of this compound could not be confirmed by isolation. The residue insoluble in hot acid contains graphite, together with the carbide,  $\text{Cr}_3\text{C}_2$ , which, after extraction of the graphite, is obtained 99–99.5% pure. The three constituents,  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_4\text{C}$ , and graphite, can be identified in microscopic sections, which show no eutectic. Possibly above  $2256^\circ$  a higher carbide,  $\text{CrC}$ , is formed.

The carbide,  $\text{Cr}_5\text{C}_2$ , is resistant to all acids. It is darker in appearance than  $\text{Cr}_3\text{C}_2$ , has  $D_4^{20} = 6.683$ , and melts at about  $1890 \pm 10^\circ$ . In the molten condition, it reduces magnesia, alumina, and zirconia, and apparently undergoes partial decomposition when melted into  $\text{Cr}_3\text{C}_2$  and graphite. It is decomposed by chlorine at a red heat, forming chromium trichloride and amorphous carbon.

The chemical composition of the alloys rich in carbon is unaffected by the rate of cooling, but larger crystals are developed when the rate of cooling is retarded. An alloy saturated with carbon boils at about  $2570^\circ$  under 8–14 mm. pressure, the vapour being pure chromium.

From the data obtained, the equilibrium diagram for the system chromium–carbon has been constructed. E. H. R.

**Metastannic Acid and its Compounds.** AUGUST KLEIN-SCHMIDT (*Monatsh.*, 1918, 39, 149–178).—On account of the discrepancies in the literature concerning the action of nitric acid on tin, a reinvestigation has been made. If nitric acid is diluted with 1½–2 volumes of water, the only product is stannous nitrate, and with stronger, and even undiluted, acid at  $0$ – $15^\circ$ , the formation of stannous nitrate can still be observed, accompanied by

normal or basic stannic nitrate; within the stated range of temperature, the yellowish-white precipitate which may be formed consists of a mixture of white stannic nitrate soluble in water with insoluble, yellowish-white basic stannic nitrate. Stannic nitrate even at the ordinary temperature slowly changes into the meta-salt, and for this reason the white, bulky precipitate which it yields with aqueous sodium hydroxide may not dissolve completely in an excess of the reagent; at  $45^{\circ}$ , the change in the stannic nitrate is so rapid that the solution suddenly gelatinises, and, after prolonged heating at  $100^{\circ}$ , the transformation is complete. The powdery product of oxidation of tin with hot nitric acid, commonly described as metastannic acid, is really a nitrate of metastannic acid which, on washing with water, gives rise to metastannic acid as a secondary hydrolytic product. Metastannic acid, obtained by the action of nitric acid (D 1.40) on tin and careful washing with water, when dried in air at the ordinary temperature has the composition  $5\text{H}_2\text{SnO}_3 \cdot 4\text{H}_2\text{O}$ , the  $4\text{H}_2\text{O}$  being lost on storage over sulphuric acid in a vacuum for several days; the nitric acid is removed only with difficulty, and if alcohol is used instead of water, the washing has to be still more prolonged; the primary oxidation product is therefore in all probability a metastannic nitrate which yields metastannic acid by hydrolysis. Metastannic acid shows no double refraction under the polarisation microscope and is an amorphous powder; it is capable of combining with hydrochloric acid or sulphuric acid with development of heat, the resulting compounds being very easily hydrolysable. The quinque-molecular formula for the anhydrous acid is confirmed by an analysis of sodium metastannate, produced by the action of sodium hydroxide on metastannyl chloride, the resulting compound having the composition  $5\text{SnO}_2 \cdot \text{Na}_2\text{O} \cdot 4\text{H}_2\text{O}$ . The parastannic acid described by Engel (A., 1898, ii, 29) is ordinary metastannic acid. Metastannic nitrate, prepared by the action of hot nitric acid on tin, has the composition  $5\text{SnO}_2 \cdot 2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , whether dried in a vacuum over sodium hydroxide and calcium chloride or between porous tiles in the air; the compound obtained from tin and cold nitric acid probably consists of a mixture or compound of stannyl nitrate,  $\text{SnO}(\text{NO}_2)_2$ , and the above metastannic nitrate; both nitrates gradually decompose in ultra-violet light with liberation of nitric acid. The action of hydrochloric acid on metastannic acid yields a stannyl chloride which, after being washed free from soluble tin salts by diluted hydrochloric acid and dried in a vacuum over sodium hydroxide and calcium chloride, has the composition  $5\text{SnO}_2 \cdot 2\text{HCl} \cdot 3\text{H}_2\text{O}$ ; the primary, pasty product, on account of its content of free acid, gives a clear solution in water, but when dry does not dissolve entirely on account of hydrolysis. As simple  $\alpha$ -stannic acid and the  $\beta$ -metastannic acid are colloidal substances capable of reversible inter-transformation, the change occurring more readily, however, from the  $\alpha$ -acid to the meta-acid, these facts accord well with the respective formulæ  $\text{H}_2\text{SnO}_3$  and  $(\text{H}_2\text{SnO}_3)_2$ ; the structure of the latter is represented by a cyclic skeleton con-

taining five tin atoms and five oxygen atoms, arranged alternately with ten hydroxyl groups attached in pairs at each tin atom. The stannyl chloride is therefore represented as  $\text{Sn}_5\text{O}_5(\text{OH})_8\text{Cl}_2$ , the metanitrate as  $\text{Sn}_5\text{O}_5(\text{OH})_8(\text{NO}_3)_2$  and the metasulphate as  $\text{Sn}_5\text{O}_5(\text{OH})_8\text{SO}_4$ .  
D. F. T.

**Presence of Vanadium and Arsenic in the Subterranean Waters of Bell-ville (Cordoba).** ATILIO A. BADO (*Bol. Acad. Nac. Ciencias, Cordoba*, 1918, **23**, 85—96).—An account of analyses of water from the district of Bell-ville, in Argentina.  
A. J. W.

## Mineralogical Chemistry.

**Hydrothermal Mineral Formation.** WOLF J. MÜLLER and J. KOENIGSBERGER (*Zeitsch. anorg. Chem.*, 1918, **104**, 1—26).—The investigations described in an earlier communication have been continued (A., 1906, ii, 553). The experiments have been confined to the system  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , with or without carbon dioxide. The starting materials used were potassium silicate (potassium water glass) and an aluminium hydroxide hydrogel, or in some cases a 0.5 molar solution of potassium aluminate. Carbon dioxide was added either as potassium carbonate or as solid pellets just before closing the bomb. The several constituents in the proportions required were heated for varying lengths of time (12 to 180 hours) at temperatures varying from  $100^\circ$  to  $440^\circ$  in a strongly made bomb. Inside the bomb was a filter tube, so arranged that by inverting the furnace the liquid contained in the bomb could be filtered into this tube, and any crystals separating subsequently collected and examined. The products were identified generally by optical methods.

On few occasions were any crystals obtained in the filter tube, the only products identified being quartz, orthoclase, zeolite, and pectolite, not leucite or nepheline. With rising temperature, the quantity of leucite in the solid phase diminishes, that of orthoclase increasing. From the slight amount of filter-tube product obtained, it is clear that the concentration of potassium aluminium silicate in the water at the temperatures employed is low, and is not likely appreciably to affect the critical temperature of the water.

Potassium felspar was only identified when the temperature used was  $360^\circ$  or above. This critical temperature ( $360 \pm 20^\circ$ ) should be an important fixed point for the geological thermometer. The presence of carbon dioxide or of sodium or calcium ions introduced in the form of labradorite does not affect the critical temperature. Albite was not observed up to  $430^\circ$ , but Baur has obtained

it under similar conditions at 450° (A., 1911, ii, 991). In presence of carbon dioxide at 310°, quartz alone is stable, the aluminosilicates appearing to be transitional with short heating at lower temperatures, forming again with longer heating at higher temperatures. The succession of minerals observed in nature is in better agreement with the results of experiments in which much carbon dioxide was present than in those without.

The formation of zeolites in absence of carbon dioxide commences below 100° and may increase up to 400°, but probably their limit of stability, with the exception of analcime, is below 300°.

The opinion is confirmed that, in hydrothermal syntheses below 400°, equilibrium is seldom attained. E. H. R.

**Meteoric Iron from Chili (Dehesa).** F. BERWERTH (*Tsch. Min. Mitt.*, 1917, 34, 272).—This mass was described by Daubrée in 1868, and was stated by Domeyko to have been found in the Cordillera de la Dehesa, near Santiago. From its compact appearance and Domeyko's analysis (Ni 14%), it was placed in the group of nickel-rich 'compact irons.' Microscopical examination of an etched surface shows, however, that the structure is octahedral. The following new analysis (mean of two by E. DITTLER) was therefore made, showing that this iron belongs to the group of very fine octahedrites.

Fe.	Ni.	Co.	Insol. (Schreibersite).
87.40	11.97	0.56	0.07

L. J. S.

## Analytical Chemistry.

**Calculation of the Possible Error in Gravimetric Estimations.** V. ZOTIER (*Bull. Sci. Pharmacol.*, 1917, 24, 298—302; from *Chem. Zentr.*, 1918, i, 945).—In the gravimetric estimation of the amount,  $x$ , of a substance,  $X$ , dissolved in water by conversion into an insoluble substance,  $Y$ , and weighing the quantity of the latter,  $y$ , the possible total error, exclusive of that due to the personal factor, is exactly equal to the algebraic sum of the individual errors. If  $m_1$  and  $m_2$  are the molecular weights of  $X$  and  $Y$ , respectively,  $\Delta m_1$  and  $\Delta m_2$  the accuracy of their determination (the value 0.16 being considered exact as fundamental), the relative error is expressed by the following relationship:

$$\Delta x/x = (m_2 y \cdot \Delta m_1 + m_1 y \cdot \Delta m_2 + m_1 \cdot m_2 \Delta y) / (x \cdot m^2_2).$$

The estimation of sulphuric acid by weighing the barium sulphate formed is chosen as example; the possible sources of error are the solubility of the sulphate in water, adhesion of the precipitate to the glass, adhesion of foreign matter to the precipitate,

the weight of dust falling on the precipitate during the estimation, increase in weight of the crucible by deposition of moisture, errors in weighing, and loss during incineration. Of these, the solubility and the error in weighing can be mathematically treated; the others are, in part, independent of  $y$ , and their sign and magnitude can only be arbitrarily estimated. In the case given above, the uncertainty is calculated to be 11:1000.

H. W.

**Colorimetric Determination of the Reaction of Bacteriological Media and other Liquids.** G. D. BARNETT and H. S. CHAPMAN (*Amer. J. Pharm.*, 1918, **90**, 592—595).—The method depends on the superimposing of two extreme colours of the indicator, as first proposed by Salm (A., 1906, ii, 218). For example, in the case of a phenolsulphonephthalein solution, the observed colour may be regarded as being composed of a definite amount of red with a definite amount of yellow, and may be matched by superimposing the extreme red and extreme yellow of the indicator in proper concentrations. If five drops of a solution of this indicator be added to a tube containing 5 c.c. of dilute acid, and five drops to another tube containing 5 c.c. of dilute alkali, the colour observed by transmitted light through both tubes will be half-way between the yellow and the red. This is the half-transformation point, and is a definite constant for this indicator. By partitioning the ten drops of indicator in varying proportions between tubes containing the same amounts of acid and alkali, and viewing each pair by transmitted light, a series of colours covering the range of usefulness of this indicator (6.9 to 8.1  $p_H$ ) will be obtained. By standardising the series by comparison with solutions of known hydrogen-ion concentration, it may be used as a colour standard for the determination of unknown reactions.

C. A. M.

**Simple Application of the Volhard Principle for the Estimation of Chlorides in Blood Plasma.** W. C. RAFFLE (*J. Biol. Chem.*, 1918, **35**, 509—512).—The citrated plasma is diluted with water, the chlorides precipitated by a standard solution of silver nitrate, and, after filtration, the excess of silver titrated by potassium thiocyanate, using iron ammonium alum as an indicator. Employing a silver nitrate solution of such a strength that 1 c.c. is equivalent to 2.5 mg. of sodium chloride, and a thiocyanate solution of one-fifth of the strength of the silver nitrate solution, the error in the estimation of the chlorides in 2 c.c. of the plasma does not exceed 1%.

H. W. B.

**Important Alteration in a Sodium Thiosulphate Solution.** H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 1098—1099).—From May to August, the strength of a sodium thiosulphate solution, as determined by the iodine method, altered from  $0.923 \times N/10$  to  $1.021 \times N/10$ . The author is unable to suggest an explanation of the phenomenon.

A. J. W.

**Simplified Gasometric Estimations.** ANDRÉ RENAUD (*J. Pharm. Chim.*, 1918, [vii], 18, 104—106).—To avoid frequent standardisations of the nitrometer in the estimation of nitrogen in urea, a second tube, exactly similar to the nitrometer tube, is employed. A known amount of urea is decomposed as usual in the nitrometer, and the volume of nitrogen obtained is noted. The same volume of air is then admitted to the comparison tube, and this volume is used as the standard in subsequent estimations. [See, further, *J. Soc. Chem. Ind.*, November.] W. P. S.

**A Survey of Methods for the Estimation of Nitrites and Nitrates in the same Solution.** ALICE OELSNER (*Zeitsch. angew. Chem.*, 1918, 31, 170—172, 178—179).—The various methods available for the estimation of nitrites and nitrates in presence of each other are reviewed. The colorimetric methods are suitable for water analysis. The diphenylamine-sulphuric acid reagent is available for both nitrates and nitrites, since, when diluted with a definite volume of water, it ceases to react with nitrates and shows a blue colour with nitrites. The nitrites are estimated first and then destroyed with urea and sulphuric acid or by boiling with ammonium chloride; this treatment does not affect the nitrates. Letts and Rea (*T.*, 1914, 105, 1157) recommend diphenylbenzidine. Several gasometric methods have been described, depending on the evolution and measurement of nitrogen or nitric oxide. For instance, on boiling a nitrite with ammonium chloride, nitrogen is evolved equivalent to twice that of the nitrite; the presence of nitrate has no influence. Ferrous chloride in presence of acetic acid or ferrous ammonium sulphate alone, on boiling, decompose nitrites with evolution of nitric oxide, which may be measured in a eudiometer. The subsequent addition of hydrochloric acid to the same solution causes the decomposition of the nitrates according to Schlösing's method. Nitric oxide may also be liberated first by hydriodic acid, which decomposes nitrites, and then by ferrous chloride and hydrochloric acid, which decomposes nitrates. Winogradsky prefers to estimate the nitrites by titration with permanganate, with the formation of nitrate, and then the total nitrates by Schlösing's method. In the analysis of culture media for the study of the progress of nitrification and denitrification by bacteria, the author recommends the permanganate method, the solution of nitrite being titrated into the diluted permanganate, previously acidified and warmed to 40°. Towards the end of the titration, plenty of time must be allowed between each addition, as the oxidation is somewhat slow. The total nitrogen is then determined as ammonia after reduction by zinc and iron in alkaline solution. The method gives much closer results than Winogradsky's, and is applicable to culture liquids which do not contain ferrous sulphate, which, moreover, is not essential for the growth of these bacteria.

The culture media may contain small quantities of other reducing substances which involve a constant error, generally negligible.



Citric acid is generally employed, but does not affect the nitrite titration performed in the manner described. Ammonium salts are eliminated by boiling before reduction of the total nitrate. Franzen and Löhman (A., 1909, ii, 517) have criticised the gasometric methods as applied to bacteriological work, and recommend Busch's method (A., 1906, ii, 392) for liquids containing much organic matter, based on oxidation of nitrites by peroxide and their decomposition by hydrazine sulphate, the nitrates being determined in both portions by precipitation with nitron. Methods of minor importance have been based on the precipitation of nitrites by 2:4-diamino-6-hydroxypyrimidine sulphate, and on the elimination of nitrites by esterification with methyl alcohol in presence of standard hydrochloric acid, the loss of acidity being determined. J. F. B.

**Gravimetric Estimation of Phosphates.** W. R. MUMMEY (*Analyst*, 1918, 43, 324).—Complete precipitation of phosphoric acid may be effected by a modification of Ullmann's method, in which the nitric acid solution is filtered prior to dilution to a standard volume. Phosphomolybdates are precipitated at 60° and allowed to remain for thirty minutes at 60°, whilst magnesium ammonium phosphate is precipitated at 80° and left for three hours at the ordinary temperature. C. A. M.

**The Estimation of Phosphoric Acid as Magnesium Pyrophosphate.** IV. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, 104, 53—56).—On account of the slight solubility of the two phosphates  $Mg[(NH_4)_2PO_4]_2$  and  $Mg_2(PO_4)_3$ , it is practically impossible to get true equilibrium in solution and is difficult to obtain a pure precipitate of normal magnesium ammonium phosphate (compare this vol., ii, 332). When the velocity of precipitation is retarded by allowing ammonia to diffuse slowly into an acid solution of the phosphoric acid-magnesia mixture in presence of ammonium chloride in the cold, the precipitate is practically pure  $MgNH_4PO_4$ . Experiments on the method of Schmitz, by which ammonia is added to a hot solution in presence of ammonium chloride and precipitation occurs on cooling, show that the precipitate thus produced is not pure. On ignition, part of the phosphoric acid is lost by volatilisation, and the residue is relatively rich in magnesium and poor in phosphoric acid, the errors approximately compensating one another. It is therefore inadvisable to redissolve and reprecipitate after ignition. The result obtained by this method is not affected by variations in dilution or in the quantity of ammonium chloride present. E. H. R.

**Rapid Micro-method for the Estimation of Phosphate and Total Phosphorus in Urine and Stools.** AKIRA SANO (*J. Biol. Chem.*, 1918, 35, 473—477).—The phosphate is precipitated by uranium in the presence of sodium acetate and acetic acid, alcohol being added to facilitate precipitation and filtration.

The uranium phosphate is then dissolved in acid and the solution treated with potassium ferrocyanide. A red colour is developed, the intensity of which is compared in a colorimeter with that produced in a similar manner from a standard uranium phosphate solution in hydrochloric acid.

H. W. B.

**Use of Manna in the Estimation of Boric Acid.** LILLIAN E. LES (*Analyst*, 1918, **43**, 323).—A freshly prepared solution of manna can replace glycerol in the estimation of boric acid. As a rule, about 5 grams of manna in solution are equivalent to about 25 c.c. of 80% glycerol.

C. A. M.

**Estimation of Silicon in Ferrosilicon.** P. NICOLARDOT and J. KOENIG (*Ann. Chim. anal.*, 1918, **23**, 169—173).—The ferrosilicon is fused with sodium carbonate and potassium nitrate, and the silica then estimated by the usual methods.

W. P. S.

**Estimation of Total Carbon in Various Biological Substances.** ANDRÉ RENAUD (*J. Pharm. Chim.*, 1918, [viii], **18**, 06—108).—The substance is heated with sulphuric acid and potassium dichromate, and the resulting carbon dioxide, together with other gases, is absorbed in ammoniacal calcium chloride solution. The resulting calcium carbonate is then estimated volumetrically. If ammoniacal barium carbonate is used for the absorption, the barium carbonate obtained may be converted into barium sulphate and weighed as such. [See, further, *J. Soc. Chem. Ind.*, November.]

W. P. S.

**Estimation of Potassium.** THOS. STEEL (*Analyst*, 1918, **43**, 48—349).—The hydrochloric acid solution containing the potassium, and also iron, calcium, magnesium, etc., but free from silica, is evaporated with the addition of an excess of platinum chloride, and the residue obtained is treated with a mixture of alcohol, 76, ether, 13, water, 11 parts. The precipitate is collected, washed with the alcohol-ether-water mixture, then dissolved in boiling water, and the solution boiled with an excess of sodium formate; after a few minutes, hydrochloric acid is added, the heating continued until the reduced platinum has flocculated, and the platinum then collected, washed, ignited, and weighed.

W. P. S.

**Volumetric Estimation of Barium and the Solubility of Barium Chromate in Various Aqueous Solutions.** JOHN NADDELL (*Analyst*, 1918, **43**, 287—289).—Barium chromate, as obtained in the separation of strontium and calcium, may be determined by a method analogous to that used for lead.

The precipitate of barium chromate (about 0.15 gram) is collected on asbestos in a Gooch's crucible and dissolved in 25 c.c. of strong hydrochloric acid and 75 c.c. of water, and the solution made up to 200 c.c. About 6 grams of potassium iodide are

added, and, after ten minutes, the liberated iodine is titrated with standard thiosulphate solution. It is essential that the hydrochloric acid should be cold and dilute to prevent liberation of chlorine by the chromate. The method has been used to determine the solubility of barium chromate in water and various aqueous solutions under the ordinary conditions of washing a precipitate. The results showed that for washing barium chromate, pure water is preferable to 1% ammonium acetate solution, which dissolves about four times as much of the salt as water. C. A. M.

**Method for the Separation and Estimation of Barium Associated with Strontium.** F. A. GOOCH and M. A. SODERMAX

(*Amer. J. Sci.*, 1918, **46**, 538—540).—Barium and strontium may be separated by treating the saturated solution of their chlorides with a mixture of concentrated hydrochloric acid and ether (4:1); about 50 c.c. of this mixture are required for 0.5 gram of the mixed salts. The precipitated barium chloride is then collected on an asbestos filter, washed with the hydrochloric acid-ether mixture, dried at 150°, and weighed. [See, further, *J. Soc. Chem. Ind.* November.] W. P. S.

**Volumetric Estimation of Zinc.** R. HOWDEN (*Chem. News*, 1918, 117, 322).—Zinc can be estimated volumetrically as chloride and in the absence of salts of ammonium and the heavy metals in the following way. The solution is evaporated to remove most of the free acid and then exactly neutralised by *N*/10-sodium hydroxide, using one drop of methyl-orange as indicator. The solution is then titrated further with *N*/10-sodium hydroxide, using phenolphthalein as indicator. Towards the end of the titration, the solution is boiled, and the end-point taken as that point where the pink colour remains on boiling. The method is stated to give absolutely concordant results. J. F. S.

**Analysis of Commercial Zinc.** L. BERTIAUX (*Ann. Chim. anal.*, 1918, **23**, 161—169, 181—191).—Methods are described in detail for the estimation of the following impurities in commercial zinc: lead, iron, cadmium, sulphur, carbon, copper, arsenic, and antimony. Analyses of forty-two samples are recorded. The maximum amount of copper found was 0.012%, of tin 0.576%, of iron 0.210%, of lead 2.327%, of cadmium 0.380%, of sulphur, trace, and of carbon 0.033%. Arsenic and antimony were present in traces only. [See, further, *J. Soc. Chem. Ind.*, 658A.] W. P. S.

**Separation of Traces of Copper from Solution.** J. E. SAUL and DAVID CRAWFORD (*Analyst*, 1918, **43**, 348).—The antiseptic known as quinosol (the potassium salt of 8-hydroxyquinoline-5-sulphonic acid) gives a precipitate with traces of copper. If 0.1 gram of quinosol is dissolved in 100 c.c. of water containing 0.0002 gram of copper (as a salt), a voluminous, yellow precipitate

forms within eighteen hours; the precipitate is soluble in dilute hydrochloric acid. By means of this reagent, copper may be detected in distilled water which has been stored in copper vessels. Other metals in very dilute solution do not give a reaction, but a precipitate may be obtained from a concentrated solution of a mercuric salt.

W. P. S.

**The Detection of Mercury in Urine, with Employment of a New Solvent for Mercuric Sulphide.** S. GUTMAN (*Biochem. Zeitsch.*, 1918, 89, 199—203).—The solvent in question is a solution of hydriodic acid, prepared by dissolving 5 grams of potassium iodide in 12 c.c. of 10% sulphuric acid, and diluting to 25 c.c. The urine is treated first with hydrochloric acid and potassium chlorate to destroy the organic matter. From the slightly acid solution, mercury is precipitated by hydrogen sulphide. The sulphide is purified by dissolving in aqua regia and reprecipitation with hydrogen sulphide. This precipitate, if it is mercuric sulphide, should be insoluble in hot nitric acid solution, but soluble in aqua regia and the given solution of hydriodic acid.

S. B. S.

**Adsorption of Colloidal Hydroxides.** K. SCHERINGA (*Pharm. Weekblad*, 1918, 55, 1070—1074).—The author considers that in analysis the adsorption of ordinary salts by metallic hydroxides has not much practical significance. In separating iron, a large excess of alkali is undesirable.

A. J. W.

**Precipitation of Iron by Hydrogen Sulphide.** R. WINDERLICH (*Zeitsch. physikal. Chem. Unterr.*, 1917, 30, 254; from *Chem. Zentr.*, 1918, i, 814).—It is commonly stated that hydrogen sulphide does not produce a precipitate in solutions of ferrous salts. This is so only in solutions in mineral acids. Even Gay-Lussac mentioned that in the presence of sodium acetate a precipitate of ferrous sulphide is obtained. Ferrous sulphide is also precipitated from solutions of ferrous acetate in acetic acid and of iron powder in citric or succinic acid.

C. S.

**Use of Titanium Trichloride as a Reducing Agent in the Estimation of Iron by Titration with Permanganate in Hydrochloric Acid Solution.** L. BRANDT (*Chem. Zeit.*, 1918, 42, 433—434, 450—451).—Titanium trichloride solution may be used in place of stannous chloride solution for the reduction of ferric salts previous to the titration of the latter with permanganate solution. The ferric salt may be reduced by the addition of exactly the requisite quantity of the titanium trichloride solution, or an excess may be added, and this excess then removed by means of copper sulphate. The presence of platinum chloride, potassium dichromate, or arsenic acid in the ferric salt solution does not affect the results. Copper sulphate may also be used for removing excess of stannous chloride when this is employed for reducing the ferric salt.

W. P. S.

**The Colorimetric Estimation of Cobalt.** E. GABRIEL JONES (*Analyst*, 1918, **43**, 317—319).—Small quantities of cobalt (0.01 to 0.1%) may be colorimetrically estimated by means of a solution of  $\alpha$ -nitroso- $\beta$ -naphthol, as used by Atack (*A.*, 1915, ii, 652), ammonium citrate solution being added to eliminate the effect of moderate quantities of many other metals. In the case of varnishes, a solution of the ash from the sample in hydrochloric acid is treated with the reagents, and the coloration compared with those given by different quantities of a standard solution of cobalt containing the same amounts of ammonium citrate and  $\alpha$ -nitroso- $\beta$ -naphthol. About 0.1 mg. of cobalt is the most satisfactory quantity for the comparison. It is essential that the solutions should contain about the same amount of free ammonia. Iron, zinc, and lead do not interfere with the estimation, but copper, nickel, or manganese, if present in notable quantities, must be removed prior to the estimation. C. A. M.

**Estimation of Tin in High-grade Wolfram Ores, and the Use of Lead as a Reduction Agent in Pearce's Assay.** A. R. POWELL (*J. Soc. Chem. Ind.*, 1918, **37**, 285—287T).—One gram of the finely ground sample is added to 5 grams of fused "bisulphate," the mixture heated to redness, then cooled, and boiled with about 80 c.c. of 5% tartaric acid solution. The insoluble portion is collected, washed with hot water, ignited while wet in an iron crucible and fused with sodium peroxide, and the tin estimated in the usual way. Traces of tin remaining in the tartaric acid solution may be recovered by means of hydrogen sulphide. The results obtained are trustworthy and agree with those found by the aqua regia method, the potassium cyanide fusion method, and the sodium peroxide fusion method. Lead may be used for the reduction of stannic salts. The solution from the sodium peroxide fusion is rendered slightly acid with hydrochloric acid, diluted to 100 c.c., 20 grams of sodium chloride, 40 c.c. of concentrated hydrochloric acid and 10 grams of granulated lead are added, and the solution is boiled for twenty minutes after the disappearance of the ferric chloride colour. A piece of marble is then added, the solution cooled, diluted with 50 c.c. of dilute sodium hydrogen carbonate solution, and titrated with iodine solution without removing the excess of lead. W. P. S.

**Quantitative Estimation of Vapours in Gases. A Differential Pressure Method.** HAROLD S. DAVIS and MARI DAVIDSON DAVIS (*J. Ind. Eng. Chem.*, 1918, **10**, 709—712).—The method depends on the fact that the vapour pressure from a liquid is independent of the kind of gas above it, provided the gas is inert (Dalton's law of partial pressure); deviations from this law are known, but it holds in the case of benzene and air. If two flasks are connected by a manometer, one of the flasks containing air and the other a mixture of air and benzene vapour corresponding with a pressure less than the saturation pressure

and a small bulb of benzene is broken in each flask, the liquid benzene in the second flask will add only the amount of pressure necessary to bring its pressure up to saturation; the benzene in the flask containing air only will, however, produce the total saturation pressure, and the manometer will register a difference in pressure equal to the pressure of the vapour in the original gas mixture.

W. P. S.

**Application of the Differential Pressure Method to the Estimation of Benzene and the Total Light Oil Content of Gases.** HAROLD S. DAVIS, MARY DAVIDSON DAVIS, and DONALD G. MACGREGOR (*J. Ind. Eng. Chem.*, 1918, 10, 712—718).—Details of procedure are given for the application of this method (preceding abstract) to the estimation of benzene, toluene, and xylene in gases.

W. P. S.

**Absorption of Light Oils from Gases.** HAROLD S. DAVIS and MARY DAVIDSON DAVIS (*J. Ind. Eng. Chem.*, 1918, 10, 718—725).—The vapour pressure of benzene from its solution in oil is governed by Henry's law for the solubility of gases in liquids and by Babo's law for the constancy of the fractional lowering of the vapour pressure from a solution over variations in temperature, and the flow of oil necessary to remove completely the benzene from a gas may be calculated accordingly. Determination of the molecular weight of an oil when dissolved in benzene is suggested as a method for standardising oils as regards their efficiency for absorbing vapours from gases.

W. P. S.

**Estimation of Alcohol in Spirituous Liquors.** NAGENDRA CHANDRA NAG and PANNA LAL (*J. Soc. Chem. Ind.*, 1918, 37, 1907).—A known weight of the alcoholic liquid is treated in a graduated cylinder with an excess of anhydrous potassium carbonate, 5 to 10% of water being added if the alcohol content is more than 90%; the mixture is then shaken and allowed to remain, or it may be subjected to centrifugal action. It separates into three layers: a lower layer of solid potassium carbonate, a middle layer of saturated potassium carbonate solution, and an upper layer of alcohol hydrate,  $4C_2H_5.OH.H_2O$ , which contains 14.061% of alcohol by volume or 91.089% by weight. The percentage quantity of alcohol in the sample is

$$(V + v \times 0.00275)[1 - 0.001068(t - 15.6)] \times 0.7936 \times 94.06/W.$$

$V$  is the volume, in c.c., of the alcohol hydrate observed,  $v$  the volume of the saturated potassium carbonate solution,  $t$  the temperature,  $W$  the weight in grams of the sample taken, 0.00275 is the solubility (in c.c.) of the alcohol hydrate per c.c. of the saturated potassium carbonate solution, 0.001068 the apparent coefficient of expansion of alcohol hydrate, and 0.7936 is the  $D_{15.6}^{15.6}$  of absolute alcohol.

W. P. S.

**A New Reaction for Acetylcarbinol.** OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1918, 89, 279—280).—A dilute solution of acetylcarbinol in water containing sodium hydroxide is boiled for a few minutes with *o*-aminobenzaldehyde. The mixture is then cooled, acidified, and made alkaline again with sodium hydrogen carbonate. A fluorescent solution is obtained, from which 3-hydroxy-2-methylquinoline can be extracted by ether; on distilling off the ether, it is obtained as a white residue, which gives a deep red colour with ferric chloride in alcoholic solution. The alcoholic solution also gives a brilliant blue fluorescence on dilution with water. These two reactions are characteristic.

S. B. S.

**The Detection of Sucrose in Milk.** G. D. ELSDON (*Analyst*, 1918, 43, 292—293).—The most sensitive test for sucrose in milk is a modification of Gayaux's test, in which 15 c.c. of the milk are treated with 1 c.c. of 3*N*-hydrochloric acid and 0.5 gram of resorcinol. On drying five drops of the resulting mixture on a white tile on the water-bath, a red coloration is obtained in the presence of as little as 0.02% of sucrose.

C. A. M.

**Titration of Oxalic Acid by the Conductance Method.** HERBERT S. HARNED and CLINTON N. LAIRD (*J. Amer. Chem. Soc.*, 1918, 40, 1213—1218).—The electrical conductivity method affords a means of titrating a strong acid in presence of much weaker acids, and as a result of observations on the change of conductivity which occurs when a solution of oxalic acid is titrated with sodium hydroxide, it is found that the replacement of the first hydrogen atom by sodium is indicated very sharply by the conductivity. The influence of dilution on the sharpness of the change in the conductivity at the point at which the acid oxalate is formed has been examined, and it appears that the abruptness of the change increases with the dilution. The presence of carbonate in the hydroxide solution leads to high results when the conductance method is used in the estimation of oxalic acid. [See further, *J. Soc. Chem. Ind.*, 653A.]

H. M. D.

**Separation of Oxalic Acid from Tartaric Acid.** ARMINUS BAU (*Chem. Zeit.*, 1918, 42, 425—426).—The solution, containing not more than 0.2% of oxalic acid, is treated with boric acid and one-fifth of its volume of calcium acetate solution, the mixture is kept in an ice-chest for forty-four hours, the precipitate of calcium oxalate then collected, washed, ignited, and the resulting calcium oxide titrated with *N*/10-hydrochloric acid. The volume of the filtrate and of the wash water must be noted; the solubility of calcium oxalate in the filtrate is equivalent to 3.42 mg. of oxalic acid per litre, whilst in the wash water it is equivalent to 4.64 mg. of oxalic acid per litre. The weight of oxalic acid found is corrected accordingly. The calcium acetate solution used is made by adding 500 c.c. of a solution of 330 grams of sodium acetate

in 300 c.c. of water to 25 grams of calcium chloride dissolved in 500 c.c. of 50% acetic acid; the mixture is kept at 7° for forty-eight hours, and then filtered. The amount of boric acid required to prevent the precipitation of calcium tartrate is at least 0.25 mol. of boric acid expressed in terms of tartaric acid, but a large excess of boric acid does not interfere.

W. P. S.

**Detection and Identification of Malonic Acid.** BOUGAULT (*Ann. Chim. anal.*, 1918, **23**, 154—155).—Malonic acid condenses with cinnamaldehyde to form cinnamylidenemalonic acid, a yellow compound, m. p. 208°, practically insoluble in water (compare Riiber, A., 1904, i, 894). A mixture of 0.10 gram of malonic acid (or an equivalent quantity of its sodium or calcium salt), 15 drops of cinnamaldehyde, and 1 c.c. of acetic acid is heated at 100° in a sealed tube for ten hours. The mixture is then diluted with 15 c.c. of water, the solution saturated with sodium carbonate, filtered, and the filtrate acidified with hydrochloric acid; the yellow precipitate formed is collected, dried at 100°, and weighed. Each gram of malonic acid yields approximately 1.10 gram of cinnamylidenemalonic acid. Oxalic acid, succinic acid, citric acid, sodium chloride, or potassium sulphate do not interfere with the reaction.

W. P. S.

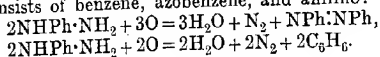
**Estimation of Indigotin.** WILHELM HEINISCH (*Färber-Zeit.*, 1918, **29**, 183—184, 194—197).—The most suitable method for the estimation of indigotin in indigo is by titration with permanganate. Constant values for the oxygen consumed are only obtained by performing the titration in highly dilute solutions, from 1 part of indigotin in 20,000 of water, onwards. The constant value does not represent the oxidation of 1 molecule of indigotin by 2 atoms of oxygen with the formation of isatin, as was formerly supposed, but corresponds with the production of a complex oxidation product resulting from the action of 9 atoms of oxygen on 5 molecules of indigotin. Thus 263 parts of indigotin require 28.8 parts of oxygen, or, in other words, 1 mg. of potassium permanganate oxidises 2.3 mg. of indigotin. Using this ratio as the basis of the standard permanganate solution, it is possible to dispense with the usual practice of standardising the permanganate against a sample of indigotin of known purity; ferrous ammonium sulphate or an oxalate may be employed. The residual colour of the oxidised indigo solution ranges from yellow to reddish-brown, and the exact end-point cannot be established by ordinary direct titration. Accurate results may, however, be obtained by a process of colour matching. The titration is carried out simultaneously in duplicate nearly to the end-point, a faint green. Permanganate is then added alternately in small quantities to each of the solutions, which are compared against a white ground after each addition, until one sample shows no green tone and the other still retains a visible trace. [See, further, *J. Soc. Chem. Ind.*, 648A.]

J. F. B.



**Colour Reaction of Mercury Fulminate with Phenylhydrazine.** A. LANGHANS (*Zeitsch. angew. Chem.*, 1918, 31, i, 161—163).—On treating mercury fulminate with phenylhydrazine, decomposition takes place, and on subsequently diluting the liquid with alcohol and adding a dilute acid, preferably sulphuric acid, a reddish-violet coloration is produced. This reaction may be used as a sensitive test for mercury fulminate. The dye can be extracted with chloroform, and its reactions indicate that it is pararosaniline. It is probable that the mercury plays a part in the reaction, since several mercury salts have been used in the preparation of rosaniline.

When phenylhydrazine is decomposed with chloride of lime, crystals of azobenzene and a yellowish-brown oil are produced. The oil consists of benzene, azobenzene, and aniline:



[See also *J. Soc. Chem. Ind.*, 1918, 637A.]

C. A. M.

**Simple Apparatus for the Estimation of Urea in Blood.** C. N. PELTRISOT (*J. Pharm. Chim.*, 1918, [vii], 18, 73—80).—A small nitrometer is described for the estimation of nitrogen by the hypobromite method; it is constructed from a 30 c.c. glass bottle and a piece of graduated tubing, 8 cm. in length and 7 mm. in diameter.

W. P. S.

**Estimation of Creatinine and Creatine in Blood.** W. DENIS (*J. Biol. Chem.*, 1918, 35, 513—516).—Accurate results for creatine and creatinine in the blood can be obtained by Folin's method (A., 1914, ii, 505) if the proteins are first precipitated by metaphosphoric acid.

H. W. B.

**Detection of Ergotinine.** LUDWIG WOLTER (*Chem. Zeit.*, 1918, 42, 446).—An alcoholic solution of ergotinine containing 1 part in 1,240,000 gives a distinct reaction with the potassium mercuric iodide reagent for alkaloids. The yellowish-red zone, changing to violet and then to blue, given by a solution of ergotinine on the addition of sulphuric acid, is characteristic of this alkaloid (Tanret). In Rosenthaler's and in Keller's modifications of the test, a trace of ferric chloride is present. It is essential that all these tests, and especially that of Tanret, should be applied under definite conditions, and in particular that the solution of the alkaloid must not be too concentrated, or zones of other colours than blue will be obtained. The hypothesis that the coloration is due to oxidation was confirmed by the fact that a trace of hydrogen peroxide could replace ferric chloride in the test. With this modification, the reaction is rendered twice as sensitive as Tanret's original test. [See also *J. Soc. Chem. Ind.*, 1918, 671A.]

C. A. M.

**The Value of Tanret's Reagent for the Detection of Quinine in Urine.** G. PÉPIN (*Bull. Sci. Pharmacol.*, 1917, 24, 337—338; from *Chem. Zentr.*, 1918, i, 955).—Tanret's reagent is

unsuitable for the detection of quinine in urine, since it yields precipitates which are soluble when warmed, even in the absence of proteins and alkaloids.

H. W.

**Isolation and Estimation of Small Quantities of Quinine in Urine.** G. PÉPIN (*Bull. Sci. Pharmacol.*, 1918, 25, 19—22; from *Chem. Zentr.*, 1918, i, 955).—The quinine is isolated by repeated extraction with small quantities of chloroform, purified, and dissolved in a few c.c. of water acidified with hydrochloric acid; the alkaloid is converted into a derivative which is soluble in water, and estimated by measuring the quantity of the solvent necessary for complete solution. The hydrate is suitable for amounts of 2—3 mg. and upwards, the picrate for quantities of less than 1 mg. Distinct fluorescence is observed with more than 1/20 mg. dissolved in water (2 c.c.). The presence of antipyrine and pyramidone alter the fluorescence and solubility of the picrate.

H. W.

**Estimation of Purine Bases in Food-stuffs.** TH. VON ELLENBERG (*Biochem. Zeitsch.*, 1918, 88, 323—336).—The author describes in detail the method employed, the bases being precipitated by copper sulphate and sodium hydrogen sulphite, and the nitrogen estimated in the precipitate. The purine content of a large number of foodstuffs is given.

S. B. S.

**Combined Estimation of Tyrosine and Uric Acid in the same Solution.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, 88, 283—285).—Folin's phenol reagent is employed. It gives a colour twice as strong with tyrosine as with uric acid. The colour with the solution of the two substances is first estimated, then uric acid is destroyed by hydrogen peroxide and sodium hydroxide, then the phenol reagent is added again, under conditions specified, and the tyrosine alone is determined colorimetrically.

S. B. S.

**Detection of Bile Pigments in Serum.** A. FOUCHET (*Compt. rend. soc. biol.*, 1917, 80, 826—828; from *Physiol. Abstr.*, 1918, 3, 246—247).—Proteins are precipitated by trichloroacetic acid, and the precipitate is yellow if bile pigments are present. On exposure to air, the precipitate becomes green, the oxidation of biliverdin being accelerated by the addition of ferric chloride. The method may be used colorimetrically.

S. B. S.

**Modification of Grimbert's Method for the Detection of Biliary Pigments in Urine.** A. FOUCHET (*J. Pharm. Chim.*, 1918, [vii], 18, 19—20).—Ten c.c. of the urine are treated with 3 c.c. of 10% barium chloride solution, the mixture submitted to centrifugal action, the sediment washed, and then mixed with 1 c.c. of a reagent consisting of trichloroacetic acid, 3 grams, ferric chloride solution, 2 c.c., and water, 20 c.c. A green coloration develops within a few minutes if biliary pigments are present. The sensitiveness of the test is about 1 in 50,000.

W. P. S.

**Detection of Methylene-blue in Urine.** L. TRIBONDEAU (*Compt. rend. soc. biol.*, 1917, **80**, 882; from *Physiol. Abstr.*, 1918, **3**, 264).—Urine is acidified with acetic acid, fragments of thymol are added, and the mixture is boiled. Thymol collects on the surface, carrying with it the pigment. S. B. S.

**Approximate Estimation of Proteins in Physiological Fluids.** ROKURO NAKASEKO (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 93—112).—A preliminary account is given of an acidimetric method for estimating proteins by precipitating with picric acid in the presence of hydrochloric acid, a given diminution of acidity after precipitation corresponding with a given amount of protein. A modification of Esbach's method is also described in which the precipitation by picric acid is carried out in the presence of  $N/20$  hydrochloric acid instead of citric acid. A modification of Roberts and Stolnikov's application of the Heller test is also described. S. B. S.

**Hydrolysis of Proteins in the Presence of Extraneous Materials and the Origin and Nature of the "Humin" of a Protein Hydrolysate.** ROSS AIKEN GOETNER (*Science*, 1918, (N.S.), **48**, 122—124. Compare A., 1916, i, 681; Hart and Sure, A., 1917, ii, 111).—The author points out that the results obtained by McHargue (this vol., ii, 280) are incorrect, because he has failed to recognise that the insoluble residue obtained on digestion of caseinogen is humin, and consequently he has omitted to take into account the nitrogen in this fraction when calculating the distribution of nitrogen in the protein. Hence the general conclusion is that an accurate estimate of the distribution of nitrogen in a feeding stuff cannot be obtained by a direct application of the Van Slyke method of analysis, even when the duration of the hydrolysis is limited to twelve to fifteen hours. H. W. B.

**Acetic-Sulphuric Acid Test for Albumin.** R. LROSE (*Pedelinico*, 1918, **25**, 224; from *Physiol. Abstr.*, 1918, **3**, 223).—The test depends on the precipitation of protein by a reagent prepared by adding 100 drops of glacial acetic acid and 100 drops of a 25% solution of sulphuric acid to 100 c.c. of a 10% solution of potassium dichromate. S. B. S.

**Protein-Sugar, its Estimation.** H. BERRY and (MRE.) L. RANDOIN-VANARD (*Soc. Biol.*, May, 1918; from *J. Pharm. Chim.*, 1918, [vii], **18**, 54).—The following method is suggested for the hydrolysis of the protein-sugar compound found in blood. Fifty c.c. of the blood are mixed with 50 c.c. of 0.2% sodium chloride solution, diluted with 90 c.c. of water, and 4 c.c. of sulphuric acid, mixed previously with 10 c.c. of water are added; the mixture is then heated in an autoclave at 120° for forty minutes. W. P. S.

